The competitive adsorption of fuel-type compounds on zeolite 13X

G. Jean, P. Chantal, S. Ahmed and H. Sawatzky

Energy Research Laboratories (CANMET)
555 Booth Street
Ottawa, Ontario, Canada
K1A 0G1

Introduction

The possibility of selectively removing the nitrogenous components of fuels by adsorption on zeolite 13X was recently reported (1-2). The purpose of this work is to develop an industrial process to remove heteroatom components from synthetic crude fractions in order to decrease the need for hydrotreating or reduce the required severity of hydroteating. The emphasis has been given to nitrogenous compounds since they dictate the severity of the process. Two of the most important criteria determining the success of an adsorption process are the adsorption capacity and the degree of selectivity. As found in the first two studies using a model solution there is a large degree of discrimination between nitrogenous compounds; the extent of adsorption is inversely proportional to the size and the acidity of the compound. The overall adsorption capacity obtained with the model solution is 10%. However, when using a real naphtha the capacity obtained is much smaller, being of the order of 1-3%. One of the potential reasons for this lower capacity could be the competitive adsorption of non-nitrogenous compounds contained in the naphthas.

The present study was undertaken to investigate the degree of competition between nitrogenous compounds and other compounds mainly olefins and oxygenated compounds. Very little competition from non-nitrogenous compounds was observed. Olefins were able to compete with nitrogenous compounds only at very high concentrations.

Experimental

All experiments were performed at room temperature in a continuous-flow fixed-bed adsorption apparatus. The zeolite is dry-packed in a stainless steel column 20 cm long and 0.4 cm ID. The first series of tests were done with a zeolite dried at 160 C . The feed is pumped at a constant flow of 0.5 mL/min and samples of the effluent are collected every 5 mL and subsequently analyzed by gas chromatography.

The adsorption capacity of individual compounds was obtained using a 1 wt% solution in toluene of the desired compound. For the competitive runs a solution of 1 wt% of each compound in toluene (2 wt% total) was used.

Results and discussion

Several factors affect the magnitude of adsorption; the adsorption capacity depends on the operating conditions such as inlet concentration, bed depth, flow rate and most importantly the affinity of the sorbate for the surface. For a given set of operating conditions the capacity measures the relative affinity of the sorbate for the solid and the solution. In the first part of this study the effect of the nature of the solution on the adsorption of aniline is investigated (Table 1). The maximum capacity is obtained for a toluene solution; the extent of aniline adsorption decreases following the addition of heptane, cyclohexene and indene. It should be noted that the degree of reproducibility between packings gives an error of 10-15%. Thus the results indicate that an olefinic solution might interfere with the adsorption of the nitrogenous compounds. This could explain the results recently reported showing a large difference in adsorption capacities for two naphthas; the lowest capacity was obtained for a naphtha abnormally high in olefins (Ref. 1, Table 2; adsorption capacity of 1 wt% for the naphtha containing 62% olefins).

Table 2 presents a summary of the adsorption capacities of various compounds. The extent of adsorption seems to be proportional to the polarity and the basicity of the compound. The indene-indoline-indole series illustrates this point; the capacities for these compounds are 3.99, 13.7 and 14.81 wt% respectively. At a concentration of 1 wt%, the olefins have very little affinity

for the zeolite as indicated by their low capacities; they do interfere with the adsorption of aniline as shown in Table 3. Oxygenated compounds have a strong affinity for the zeolite. The extent of adsorption of phenol compares to those of aniline and indole, two of the most retained nitrogenous compounds. Under competition, phenol is quite successful in displacing the nitrogenous compounds (Table 4). These results suggest that naphthas high in oxygenated compounds could be treated using the adsorption process. This could be advantageous for synthetic crude naphthas such as coal derived liquids.

The study on competition between nitrogenous compounds show that the adsorption capacity of individual compounds is a good predictor of the adsorption process for a complex mixture. Indeed the order of affinity indicated by the adsorption capacity of the individual compound is very similar to the order obtained for a solution containing eighteen compounds (1). Except for a few cases the individual capacities also predicted the relative capacities for the "two compound competitions" showed in Tables 3-7. The results indicate that the total capacity obtained is of the order of 15 wt% . The adsorption is not dominated by a single nitrogenous compound.

Conclusion

The data obtained in this study show that there should be little competition from non-heteroatom compounds except possibly from olefins. Both nitrogenous and oxygenated compounds have a strong affinity for the zeolite. The adsorption of oxygenated compounds presents a real advantage since these compounds are also problematic. Oxygenated compounds are present in significant amounts in a variety of synthetic crude fractions.

An adsorption process for the removal of heteroatom components, using a zeolite 13X , would not be efficient because of the low affinity of a number of nitrogenous compounds. For instance phenetylpiperidine and collidine are adsorbed at less than 8 wt% without any competition (Table 2) . This capacity will decrease in a multi-component solution because of site competition. Future work should concentrate of finding an adsorbent that can remove the less basic compounds.

1) G. Jean, S. Ahmed and H. Sawatzky, "The Selective Removal of Nitrogenous-Type Compounds from Fuels by using zeolites", Sep. Sci. Technol. 20(7 & 8), 555-564, 1985

2) G. Jean, E. Bonvie and H. Sawatzky, "Selective Removal of Nitrogenous Compounds Using Zeolites", ACS National Meeting Chicago Sep. 8-13: Preprint Fuel Division Vol. 30(4), 474-480, 1985

Table 1

Solvent effect on aniline adsorption capacity (wt% on zeolite)
1 wt% aniline in solvent

Solvent	Capacity %	Capacity relative to toluene
toluene	22.91	——
50:50 toluene/heptane	19.28	0.84
50:50 cyclohexene	15.13	0.66
50:50 1-indene	15.09	0.65

Table 2

Adsorption capacity for individual compounds (wt% on zeolite)
1 wt% in toluene

Compound	Capacity %	Compound	Capacity
Decene	1.21	Cycloheptanone	11.70
Indene	3.99	Octylamine	11.91
1-Phenethylpiperidine	5.73	Dibenzylamine	12.99
Aminoanthrancene	5.98	Indoline	13.70
2,4,6-Collidine	7.24	4-Ethylpyridine	14.01
1,2,5-Trimethylpyrrole	8.47	Quinoline	14.45
2-Phenylpyridine	8.69	Iso-Quinoline	14.72
Phenothiazine	9.04	Indole	14.81
2,2´-Dipyridyl	10.45	Phenol	16.08
Decylalcohol	11.18	Aniline	22.91

Table 3

Adsorption capacity for various compounds in the presence of Aniline (wt% on zeolite)
1 wt% compound and 1 wt% aniline in toluene

Compound	Capacity %	Relative Capacity	Aniline capacity %	Aniline Relative Capacity	Total Capacity
Decene	0.43	0.36	16.21	0.74	16.63
Indene	1.07	0.28	13.64	0.59	14.71
Dibenzylamine	3.66	0.28	15.38	0.67	19.04
Decylalcohol	5.43	0.49	15.16	0.66	20.59
Indole	7.39	0.50	12.66	0.55	20.05
2,2´-Dipyridyl	7.77	0.74	7.67	0.34	15.44
Quinoline	8.92	0.62	11.79	0.52	21.71
Indoline	9.86	0.72	16.82	0.74	26.68

Table 4

Adsorption capacities for various compounds in the presence of Phenol (wt% on zeolite)
1 wt% compound and 1 wt% phenol in toluene

Compound	Capacity %	Relative Capacity	Phenol capacity %	Phenol Relative Capacity	Total Capacity
Dibenzylamine	3.57	0.28	10.59	0.66	14.11
Quinoline	4.75	0.44	11.80	0.73	16.55
2,2´-Dipyridyl	5.71	0.55	9.06	0.56	14.77
Indole	7.61	0.51	13.27	0.83	20.88
Decylalcohol	7.68	0.69	11.41	0.71	19.09

Table 5

Adsorption capacities for various compounds in the presence of Octylamine (wt% on zeolite)
1 wt% compound and 1 wt% octylamine in toluene

Compound	Capacity %	Relative Capacity	Octylamine capacity %	Octylamine Relative Capacity	Total Capacity
2,2´-dipyridyl	8.21	0.79	6.62	0.56	14.83
4-Ethylpyridine	8.59	0.77	4.41	0.37	13.00
Dibenzylamine	8.91	0.69	6.98	0.59	15.89
Cylcloheptanone	9.40	0.80	5.68	0.48	15.08
Quinoline	9.70	0.90	6.89	0.56	16.59
Indole	10.06	0.68	6.76	0.62	16.82

Table 6

Adsorption capacities for various compounds in the presence of 4-Ethylpyridine (wt% on zeolite)
1 wt% compound and 1 wt% 4-ethylpyridine in toluene

Compound	Capacity %	Relative Capacity	4-Ethylpyridine capacity %	4-Ethylpyridine Relative Capacity	Total Capacity
Quinoline	5.65	0.52	5.59	0.50	11.24
Decylalcohol	5.74	0.51	9.45	0.85	15.19
Dibenzylamine	5.79	0.45	9.06	0.82	14.85
Indoline	6.19	0.45	7.29	0.66	13.48
Indole	7.13	0.48	6.82	0.61	13.95
Cylcloheptanone	7.90	0.68	9.53	0.86	17.43
2´,2´-Dipyridyl	8.34	0.80	5.89	0.53	14.23
Aniline	13.97	0.61	8.32	0.75	22.29

Table 7

Adsorption capacities for various compounds in the presence of Quinoline (wt% on zeolite)
1 wt% compound and 1 wt% quinoline in toluene

Compound	Capacity %	Relative Capacity	Quinoline capacity %	Quinoline Relative Capacity	Total Capacity
Decylalcohol	1.78	0.16	9.35	0.87	11.13
Dibenzylamine	4.23	0.33	9.46	0.88	13.69
2-Phenylpyridine	5.21	0.60	9.14	0.85	14.35
Indole	5.85	0.40	7.11	0.65	12.96
Indoline	7.23	0.53	8.63	0.80	15.86
2,2´-Dipyridyl	8.05	0.77	4.37	0.40	12.42
Aniline	11.19	0.52	8.92	0.62	20.11

BIOLOGICAL MARKER AND RELATED COMPOUNDS IN
NATURAL AND SYNTHETIC LIQUID FUELS

M.G. Strachan, R. Alexander and R.I. Kagi
School of Applied Chemistry, Western Australian Institute of Technology,
Bentley 6102, Western Australia

INTRODUCTION

Molecular level characterization of synthetic crudes using GC and GC/MS techniques has typically involved identifying the major components present, irrespective of chemical class (1-4). This approach differs considerably from the application of these methods for characterizing natural crude oils. These samples are only analyzed for particular compound types whose distributions and use in selected ratios can provide useful geochemical information. The compounds studied are what are generally termed "biological markers", aliphatic components directly related to a biological precursor. These compounds include; n-alkanes, acyclic isoprenoids, diterpanes, triterpanes and steranes (5,6). More recently, however, alkyl aromatics such as dimethylnaphthalenes (7), trimethylnaphthalenes (8,9) and methylphenanthrenes (10) hae also been employed in a similar manner.

The literature contains a paucity of reports of analyses of synthetic liquids specifically for biological marker compounds (11-14). These studies, which encompass both coal- and oil shale-derived liquids, suggest that the geochemical data obtained can provide useful information about the source material and different liquefaction processes. Interestingly, the coal derived liquids examined for biological marker compounds were almost exclusively produced from bituminous coals. This is surprising in view of the much reported liquefaction reactivity of the lower ranked, lignites and brown coals. Furthermore, as the use of alkyl aromatics as geochemical indicators is only a recent innovation, the extension of this application to synthetic liquids is as yet unreported.

Two Australian fossil fuel reserves whose liquefaction potential have been extensively investigated are the massive Latrobe Valley (Victoria, Australia) brown coal deposits, and the Rundle oil shale (Queensland, Australia) seams. In fact, a 50 ton-per-day pilot plant based on the SRC I & II processes, and using these brown coals as feedstock is currently nearing completion in the Labrobe Valley. This paper reports on a study of synthetic liquids, produced from these two sources, that have been characterized by GC and GC/MS in an anologous fashion to natural crudes. For comparative purposes, the data obtained from a terrestrial crude oil and a marine crude oil are also included. In addition, the effect of liquefaction process on the respective data is illustrated by the different coal derived liquids.

EXPERIMENTAL

Samples. The coal derived liquids were all produced from a medium-light lithotype Victoria brown coal from the Loy Yang Field (bore 1277, depth 67-68m). The liquefaction processes employed were: solvent extraction (CH_2Cl_2); slow pyrolysis (50°-1000^oC at 3^oC min^{-1}); hydrogenation (tetralin/H_2 (10.3 mPa), 375^oC, 2hrs) and CO/H_2O (bed moist coal/CO (6.8 MPa), 350^oC, 2hrs). More detailed information on the liquefaction conditions and the product yields and analyses are given elsewhere (15,16).

The oil shale derived liquids were produced from the Rundle oil shale by solvent extraction (CH_2Cl_2) and by the Lurgi-Ruhrgas retorting process (17). In all cases, the synthetic liquids are operationally defined as the methylene dichloride soluble portion of the liquefaction product.

The two natural crude oils represent oils sourced from terrestrial organic matter and marine organic matter, respectively. The former is from the off-shore Gippsland Basin, Australia (the Latrobe Valley coals are part of the on-shore Gippsland Basin) and the latter, the North Sea, Denmark.

<u>Separation Procedure</u>. The sample (30mg) in methylene dichloride (2cm^3) was preadsorbed onto silicic acid using the method of Middleton (18). Upon removal of the solvent by rotary evaporation, the preadsorbed sample was placed on top of a column of silicic acid (3g). Successive elution with n-pentane; n-pentane/diethyl ether (95:5) and methylene dichloride/methanol (90:10) gave three fractions: (1) aliphatic hydrocarbons, (2) aromatic hydrocarbons and (3) heteronuclear compounds.

An aliquot of the aliphatic hydrocarbons fraction, in benzene, was subsequently treated with activated 5A molecular sieves to separate the n-alkanes from the branched and cyclic alkanes (19). Similarly, the aromatic hydrocarbons fraction was subjected to thin layer chromatography on alumina, with n-hexane as eluant, to yield a di- and trinuclear aromatic fraction (9). These fractions after appropriate reported workup procedures (19,9), and solvent removal were amenable for analysis by GC and GC/MS.

<u>GC and GC/MS analysis</u>. Gas chromatography was performed using a Hewlett-Packard (HP) 5880A chromatograph, fitted with a 50m x 0.2mm i.d. WCOT fused-silica column coated with 5% crosslinked phenylmethyl silicone (bp-5, SGE Australia). For all analyses, hydrogen was used as carrier gas at a linear velocity of 30 cm sec^{-1}, and detector (FID) and injector temperatures were 300°C and 280°C, respectively. In a typical analysis of a total aliphatic hydrocarbon fraction, the oven of the chromatograph was temperature programmed from 65°C to 280°C at 4°C min^{-1}, then held isothermal for 10 minutes. The oven temperature programme for analysis of the di- and trinuclear aromatics fractions was: 70°C for 1 minute; then 70°C to 190°C at 1°C min^{-1}; followed by 190°C to 300°C at 10°C min^{-1} and finally, held isothermal for 10 minutes. All GC analysis were integrated using the associated HP data terminal. Component identification was, in both cases, by comparison of the retention times with those of authentic isomers (8,10,19,20).

Only the branched/cyclic alkane fractions were analyzed by GC/MS. The analyses were performed using a HP 5895B capillary GC-quadrupole MS-computer data system, fitted with a 50m x 0.22mm i.d. WCOT fused-silica cross-linked methylsilicone column (Hewlett Packard). Samples for analyses were diluted to a 1% w/w solution in n-hexane and injected on-column at 50°C. The oven was then temperature programmed to 300°C at 4°C min^{-1}, and held isothermal for 20 minutes. Hydrogen was used as carrier gas at a linear velocity of 28 cm sec^{-1}. The samples were analyzed in the selected ion monitor (SIM) mode, using dwell times of 10 msec for each ion monitored. Typical MS operating conditions were: EM voltage 2200V; ionization energy 70eV; source temperature 250°C.

The ions monitored were typical of those used for crude oil biological marker studies. For example, m/z 217, 218, 259 (steranes and diasteranes); m/z 177, 191, 205 (triterpanes) and m/z 123, 193 (bicyclics and tetracyclics). Specific compounds were identified by comparison of their retention times with literature data. (21-23).

RESULTS AND DISCUSSION

Figure 1 shows gas chromatograms of the total aliphatic hydrocarbon fractions of the synthetic liquids and natural crude oils. The compound distributions evident in these chromatograms for the coal derived liquids differ markedly for the various liquefaction processes. The solvent extract is overwhelmingly dominated by triterpenoids (consistent with the higher plant input of the source material), while the hydrogenation product and pyrolysate have the n-alkanes in the highest relative abundance. It is interesting to note that this observation conflicts with that of Youtcheff and coworkers (12) who found no difference in the distributions of saturate hydrocarbons from several bituminous coal solvent extracts and their corresponding hydrogenation products. In addition, the pyrolysate also contains a homologous series of n-alkanes. The CO/H$_2$O product is quite distinctive in that it has a bimodal n-alkane distribution and appears to

contain a major group of components which have retention times between $n-C_{22}$ and $n-C_{23}$. The oil shale derived liquids can also be differentiated from each other. The solvent extract is predominantly n-alkanes, having the C_{27} member as the most abundant component; while the retort oil is much more complex. Although it has the n-alkanes as the most abundant homologous series, it also contains a series of n-alkenes. However, it differs from the coal pyrolysate in having its n-alkane and n-alkene distributions maximising at lower carbon numbers. In fact, the general shapes of the n-alkanes distributions for the coal pyrolysate and oil shale retort are very similar to those for the terrestrial and marine crudes, respectively. This may suggest that the geochemical processes generating natural crudes are pyrolytic in nature.

Two geochemical indicators determined from chromatograms of the total aliphatic hydrocarbons are the Carbon Preference Index (CPI) and Pristane/Phytane ratio (Pr/Ph). The former is based on the n-alkanes, and the latter, the C_{18} and C_{19} acyclic isoprenoids. The CPI values for the oil shale derived liquids are much higher than those for both the coal derived liquids and natural crudes. Except for the solvent extract, the CPI values for the coal derived liquids are all less than unity, with that for the CO/H_2O product being appreciably so. Interestingly, the CPI values for the two natural crudes are almost identical. However, it is the Pr/Ph ratio values that clearly distinguish the coal derived-from the oil shale derived liquids, and the torrestrial from the marine crude. Both the coal derived liquids and the terrestrial crude have considerably higher values of this ratio than their corresponding counterparts. The similarities of values for the coal derived liquids and the terrestrial crude, and the shale derived liquids and the marine crude is not surprising, considering their respective source organic matter. The combined use of CPI and Pr/Ph does, hence, suggest that coal- and oil shale-derived liquids can be differentiated from each other and their respective natural counterparts.

Further confirmation of this possibility is afforded by GC/MS analyses of the respective branched/cyclic fractions. Table 1 presents the data for selected geochemical indicators based on several biological marker compounds. Typical mass fragmentograms of steranes (m/z 217) and triterpanes (m/z 191) are illustrated in Figure 2, for the coal pyrolysate and terrestrial crude oil. Component identification is given in Table 2. The mass fragmentograms show that the samples generally contain the same components, with differences being mainly in individual relative abundances. However, the m/z 191 mass fragmentograms do provide a ready means of distinguishing synthetic from natural crudes. The differences are most apparent in the high relative abundances of: 1) C_{29} to C_{30} $\alpha\beta$-hopanes (peaks F and D, respectively, in Fig. 2a) and 2) the C_{27} β-hopane (peak C in Fig. 2a) for the synthetic liquids compared with the natural crudes.

Kaurane is an unequivocal biological marker for higher plant material in fossilized organic matter (24). The epimer ratio (Table 1) is, therefore, useful for distinguishing the oil shale derived liquids and the marine crude from the coal derived liquids and the terrestrial crude. In fact, the respective values for the coal derived liquids and the terrestrial crude suggest, they too can be differentiated from each other.

The values for the drimane epimer ratios are similar for all the synthetic liquids, but are significantly lower than those for the natural crudes, whose respective values are almost identical. Conversely, the $\beta\beta/\alpha\beta$ hopane ratios and the moretane/hopane ratios are considerably higher for the synthetic liquids than for their natural counterparts. Again, it is difficult to distinguish, unambiguously, between the oil shale and coal derived liquids. However, these drimane and hopane (moretane) based parameters do permit unequivocal distinction between the natural and synthetic crudes. Similarly, the sterane epimer ratios are significantly different between the synthetic liquids and the natural crudes; the values

for the ratio being much higher in the latter. However, in natural crudes the above parameters have been shown to be maturity dependent; therefore, synthetic liquids produced under more severe thermal conditions may show values approaching those observed for their natural counterparts. This is in fact observed with the coal hydrogenation product and the marine crude. This suggests that this parameter should not be used in isolation, although generally most natural crude oils are generated from mature source rocks and have epimeric ratios of 1.1.

In contrast, the C_{29}/C_{27} sterane ratio can be used to differentiate the coal derived liquids and the terrestrial crude, from the oil shale derived liquids and the marine crude. The values are much higher for the former, than for the latter samples. Actually, this ratio could not be determined for the shale retort oil as the C_{27} sterane was immeasurable. Again the hydrogenation product appears anomalous, with the value for this parameter being much lower than for the other coal derived liquids.

Indeed, the values for the $\beta\beta/\alpha\beta$ hopane ratio and the sterane-based parameters, for the hydrogenation product are of geochemical interest. The low relative abundance of the C_{30} $\beta\beta$-hopane, and its similarity to those in natural crudes suggests that certain maturation processes can be replicated under laboratory conditions. This is further shown by the value of sterane epimer ratio, which unlike those for other synthetic liquids, indicates a significant degree of configuration isomerization. In addition, the low value for the C_{29}/C_{27} sterane value is consistent with dealkylation of the C_{29} sterane as a result of increased thermal stress. These observations thus suggest that hydrogen transfer processes may be important in the geosphere for crude oil formation.

Inspection of the alkyl aromatic-based parameters, which are presented in Table 3, shows that they too can be employed to distinguish synthetic from natural crudes, and coal derived from shale derived liquids. Figure 3 shows a typical gas chromatogram of a dinuclear and trinuclear aromatics fraction for the coal pyrolysate and terrestrial crude. The numbered peaks, which refer to those used in defining the parameters, are defined in Table 4. The parameters DNR-2, TNR-1 and MPI-1 allow differentiation of the synthetic from the natural crudes. The values for DNR-2 in the synthetic liquids are normally much lower than those observed in natural crudes. The value for the marine crudes, presented here (i.e. 72.6) is anomalously low for oils sourced from this type of organic matter, and is a direct result of the immaturity of this particular sample. For TNR-1 and MPI-1, the synthetic liquids generally have higher values than the natural crudes. However, both the coal pyrolysate and the oil shale retort have similar values to those observed for the terrestrial and marine crudes. This may be further evidence that pyrolytic processes play a role in oil generation.

The coal derived liquids and terrestrial crude have considerably higher values of DNR-6 and TDE-1 than the oil shale liquids and marine crude. Thus, these groups of samples may be distinguished from each other using these parameters. Hence, appropriate combinations of parameters permit the origin and source type of a liquid fuel to be ascertained. For example, high DNR-2 and TDE-1 values infer the oil is a natural terrestrial crude, whereas low values for these two parameters suggest it is an oil shale derived liquid.

In conclusion, the approach outlined here shows that: 1) natural and synthetic crudes can be fingerprinted using known geochemical parameters; 2) the choice of liquefaction process can considerably alter the distribution of total aliphatic hydrocarbons for a given source material; 3) natural and synthetic crudes can be distinguished from each other, as can be their source types, using appropriate combinations of biological marker and/or alkyl aromatic-based paramters; 4) geochemical processes such as the epimerization of steranes and the depletion of $\beta\beta$-hopanes can be replicated in the laboratory and 5) pyrolytic-, together with hydrogen

transfer processes may be important in the formation of natural crude oils.

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Table 1. Geochemical Parameters based on Biological Marker Compounds.

SAMPLE	Kaurane[a] $\frac{16\beta(H)}{16\alpha(H) + 16\beta(H)}$	Drimane[b] $\frac{8\beta(H)}{8\alpha(H) + 8\beta(H)}$	C_{30}[c] Hopanes $\beta\beta/\alpha\beta$	C_{30}[d] Moretanes Hopanes $(\beta\alpha/\alpha\beta)$	C_{29}[e] Steranes 20S/20R	C_{29}/C_{27}[f] Steranes
Coal						
Solvent Extract	0.07	0.56	2.00	1.50	N.D.	N.D.
Pyrolysate	0.24	0.58	0.55	1.53	0.20	10.8
Hydrogenation	0.65	0.55	<0.05	1.38	0.58	0.8
CO/H$_2$O	0.20	0.59	0.71	1.48	0.13	17.6
Oil Shale						
Solvent Extract	N.D.	0.78	4.70	0.77	0.10	0.89
Retort	N.D.	0.50	1.01	1.82	0.11	N.D.
Crude Oils						
Terrestrial	0.99	0.99	<0.05	0.10	0.84	5.11
Marine	N.D.	1.00	<0.05	0.13	0.57	0.64

a - 16β(H)-kaurane/16α(H)-kaurane + 16β(H)-kaurane

b - 8β(H)-drimane/8α(H)-drimane + 8β(H)-drimane

c - 17β(H), 21β(H)-hopane/17α(H), 21β(H)-hopane

d - 17β(H), 21α(H)-moretane/17α(H), 21β(H)-hopane

e - (20S)-5α(H), 14α(H), 17α(H)-ethylcholestane/(20R)-5α(H), 14α(H), 17α(H)-ethylcholestane

f - (20R)-5α(H), 14α(H), 17α(H)-ethylcholestane/(20R)-5α(H), 14α(H), 17α(H)-cholestane

N.D. Not determinable

Table 2.   Identification of the Triterpanes (m/z 191) and Steranes (m/z 217) present in the
Mass Fragmentograms shown in Figs. 2a and 2b.

	Triterpanes (Fig. 2a)		Steranes (Fig. 2b)
Peak	Compound	Peak	Compound
A	17α(H), 22, 29, 30-trisnorhopane	A	20S-13β, 17α-diacholestane
B	18α(H), 22, 29, 30-trisnorneohopane	B	20R-13β, 17α-diacholestane
C	17β(H), 22, 29, 30-trisnorhopane	C	20S-24 ethyl-13β, 17α-diacholestane
D	17α(H), 21β(H)-30-norhopane	D	20R-5α, 14α, 17α-cholestane
E	17β(H), 21α(H)-30-normoretane	E	20R-24-ethyl-13β, 17α-diacholestane
F	17α(H), 21β(H)-hopane	F	20S-24-ethyl-5α, 14α, 17α-cholestane
G	17β(H), 21β(H)-30-norhopane	G	20R-24-ethyl-5α, 14β, 17β-cholestane
H	17β(H), 21α(H)-moretane	H	20S-24-ethyl-5α, 14β, 17β-cholestane
I	22S-17α(H), 21β(H)-homohopane	I	20R-24-ethyl-5α, 14α, 17α-cholestane
J	22R-17α(H), 21β(H)-homohopane		
K	17β(H), 21β(H)-hopane		
L	22S and R-17β(H), 21α(H)-homomoretane		
M	22S-17α(H), 21β(H)-bishomohopane		
N	22R-17α(H), 21β(H)-bishomohopane		
O	Unknown		
P	17β(H), 21β(H)-homohopane		
Q	22S-17α(H), 21β(H)-trishomohopane		
R	22R-17α(H), 21β(H)-trishomohopane		

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Table 3. Geochemical Parameters based on Dimethylnaphthalenes,
Trimethylnaphthalenes and Methylphenanthrenes.

SAMPLE	DNR-2[a]	DNR-6[b]	TNR-1[c]	TDE-1[d]	MPI-1[e]
Coal					
Solvent Extract	48.3	4.8	1.3	0.9	2.30
Pyrolysate	23.3	2.3	0.5	6.3	0.73
Hydrogenation	44.3	4.1	1.1	4.8	1.12
CO/H_2O	9.3	9.3	0.7	2.7	N.D.
Oil Shale					
Solvent Extract	23.1	1.9	1.3	1.6	1.08
Retort	26.1	1.2	0.8	0.3	0.80
Crude Oils					
Terrestrial	279.0	2.7	0.7	4.9	0.78
Marine	72.6	2.0	0.5	0.3	0.74

a - 2,7-dimethylnaphthalene/1,8-dimethylnaphthalene

b - 2,6- + 2,7-dimethylnaphthalenes/1,4- +2,3-dimethylnaphthalenes

c - 2,3,6-trimethylnaphthalene/1,4,6- + 1,3,5-trimethylnaphthalenes

d - 1,2,5-trimethylnaphthalene/1,2,4-trimethylnaphthalene

e - 1.5 x (2- + 3-methylphenanthrenes)/(phenanthrene)+ 1-methylphenanthrene
       + 9-methylphenanthrene

N.D. Not determinable

Table 4. Identification of the Aromatic Compounds used in the Parameters defined in
Table 2 and shown in the Gas Chromatogram in Fig. 3.

| Peak	Compound	Peak	Compound
1	2,6-dimethylnaphthalene	9	1,2,4-trimethylnaphthalene
2	2,7-dimethylnaphthalene	10	1,2,5-trimethylnaphthalene
3	1,4- and 2,3-dimethylnaphthalenes	11	phenanthrene
4	1,8-dimethylnaphthalene	12	3-methylphenanthrene
5	1,4,6- and 1,3,5-trimethylnaphthalenes	13	2-methylphenanthrene
6	2,3,6-trimethylnaphthalene	14	9-methylphenanthrene
7	1,2,7-trimethylnaphthalene	15	1-methylphenanthrene
8	1,2,6-trimethylnaphthalene		
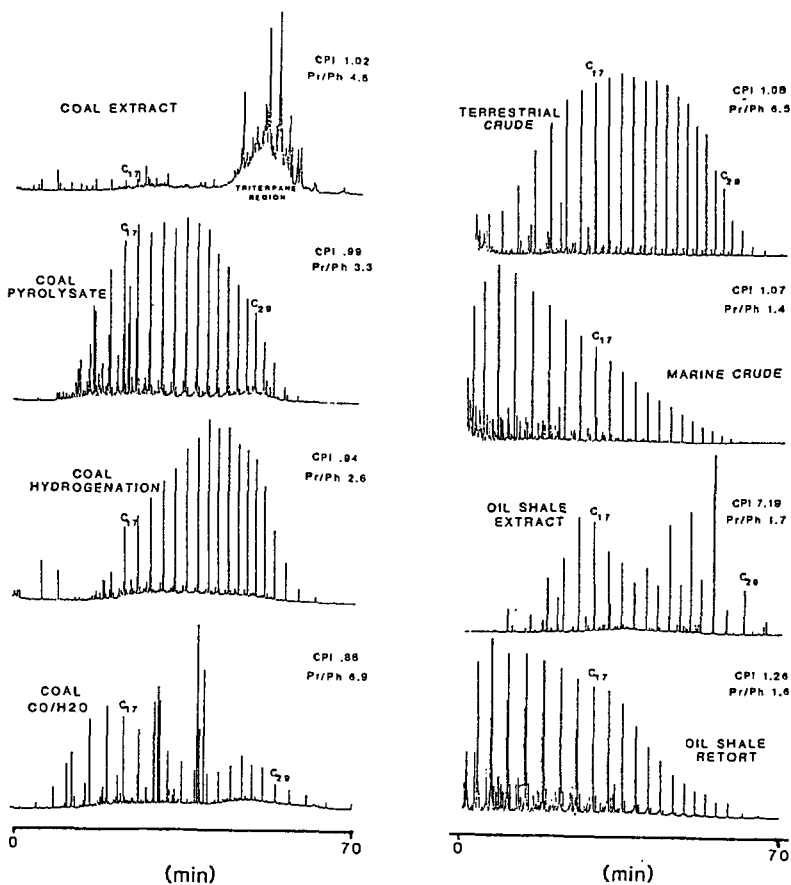
Figure 1. Gas chromatograms of the total aliphatic hydrocarbon fractions of the synthetic and natural crudes.
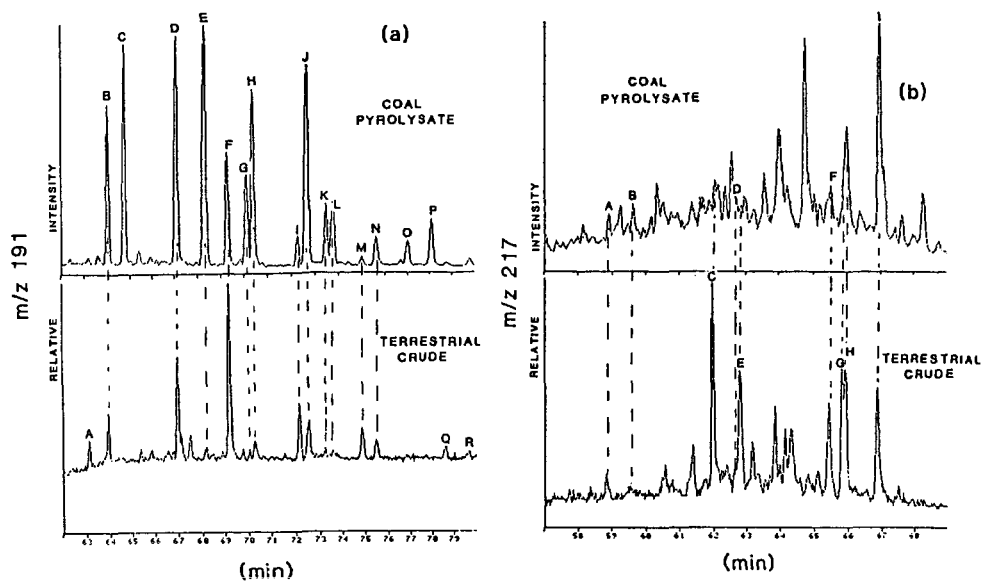
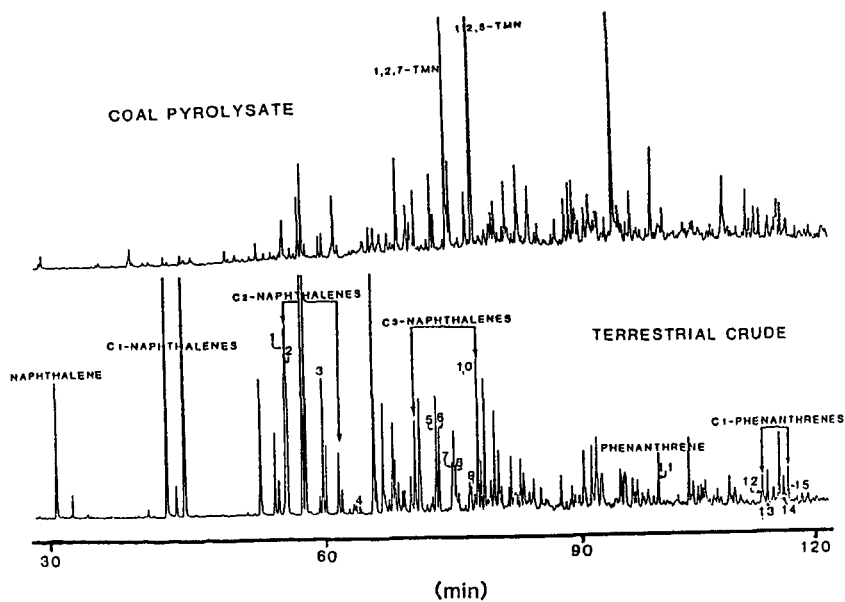Figure 2. Mass fragmentograms for (a) triterpanes and (b) steranes from the coal pyrolysate and terrestrial crude.

Figure 3. Gas chromatograms of the dinuclear and trinuclear aromatic fractions from the coal pyrolysate and terrestrial crude.

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DETERMINATION OF FUEL AROMATIC CONTENT AND ITS EFFECT ON RESIDENTIAL OIL COMBUSTION

S.W. Lee, F. Preto and A.C.S. Hayden

Canadian Combustion Research Laboratory
Energy Research Laboratories
Energy, Mines and Resources Canada
Ottawa, Ontario, Canada
K1A 0G1

ABSTRACT

The increasing use of distillate fuel oils processed from synthetic crudes has caused concern for deteriorated performance due to increased levels of aromatic compounds and increased viscosity of these fuels. The performance characteristics of middle distillate fuels of varying physical and chemical properties, derived from both conventional and synthetic crudes, are being determined on residential combustion systems at the Canadian Combustion Research Laboratory.

The aromatic properties of the fuels are determined using a range of techniques: the fluorescent indicator absorption method (FIA) for total aromatics; the proton nuclear magnetic resonance method (PNMR) for aromaticity and hydrogen distribution; the gas chromatographic/mass spectrometric (GC/MS) method and column chromatographic method for aromatic compound types; the mass spectrometric (MS) method for paraffins, olefins, naphthenes and aromatics (PONA); theoretical calculations based on physical properties for total aromatics; and aniline point measurements.

In this study 22 fuels were examined, and observations correlating the fuel aromatic properties with transient particulate emissions are presented.

INTRODUCTION

An increased awareness of dependency on the oil exporting nations and the volatility of the world oil price market has changed the outlook of the oil industry. Ever since the energy crisis of the 1970's, industry and consumers have come to realize the potential savings of implementing energy conservation measures. The North American petroleum industry has reduced energy consumption significantly in recent years and according to a 1985 survey (1) an additional 14% reduction is technically feasible. One approach, taken by refiners, is to reduce the manufacturing cost by maximizing the use of lower cost components. At the present time, this approach

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is highly attractive since good quality conventional resources are being depleted rapidly all over the world, while the global demand for middle distillates is expected to increase (2). The combined effects of energy conservation measures and the natural decline of good quality conventional feedstocks have created new concerns for refiners over fuel oil quality.

Due to cold climate and immense distances, Canada is one of the largest per capita users of oil in the world (3). As a result of these "hardships", Canadian industry and consumers face greater energy conservation challenges than almost anywhere else in the world. In addition to an overall reduction in energy consumption by the population, innovative solutions have to be considered to extend the life of the conventional resources. Such efforts include replacement of oil with alternate energy sources and development of alternate oil supplies such as those from frontier reserves, heavy oils and tar sands from western Canada. Middle distillates processed from synthetic crudes derived from the heavy oils and tar sands of Alberta and Saskatchewan are already on the Canadian market and their production is increasing. By 1990, Canadian tar sands development is expected to increase production capacity from the current 12% to 23% of Canadian crude oil demand with a future increase to 39% in the year 2005 (4). Regardless of fluctuating world oil prices, which depend on numerous unpredictable events and circumstances, it is in the industry's best interest to have at hand the technology which will best utilize the available indigenous resources.

Middle distillates processed from tar sand crudes contain higher proportions of aromatic and naphthenic compounds which can degrade combustion quality (5). The problems associated with the use of highly aromatic fuels are well known and widely documented (6 - 11). A better understanding of the relations between oil properties and their performance could help refiners to better handle such problems and allow more blending flexibility. In the case of heating oils, possible use of lower grade fractions will reduce manufacturing costs and allow diversion of more quality components into diesel fuel and gasoline. With these objectives in mind, an experimental program to study the effects of oil quality on residential oil combustion characteristics is being carried out at the Canadian Combustion Research Laboratory.

In the course of this study, it has become apparent that accurate and reliable analytical techniques for fuel property determinations are critical in order to achieve accurate correlation with performance characteristics. The suitability of the various techniques for use in petroleum refineries is also an important consideration. For example, in the determination of aromatics there are numerous methods available, but limitations associated with each technique restrict its use to certain areas. This paper describes the approaches taken to determine the aromatic content of middle distillate fuels, and presents the correlations observed between fuel aromatics and particulate emissions.

EXPERIMENTAL

Experimental facility.

Detailed descriptions of the experimental equipment and
procedures developed for the fuel quality evaluation program have
been reported elsewhere (12). Figure 1 is a schematic diagram of the
equipment used in the combustion experiments. The experimental rig
includes a commercial warm air furnace, a chilled air distribution
system, fuel conditioning unit, continuous emission analyzers, and
data acquisition and processing equipment. Special emphasis was
given to the design of the test rig so that experimental conditions
would simulate those of a "real life" residential environment.

Fuel variety.

The middle distillate oils selected for this study were
obtained from six major Canadian oil companies and from the National
Research Council of Canada. The oils include commercial No. 2 fuels,
No. 2 fuels processed from synthetic crudes, light gas oils, light
cycle oils, jet fuels, diesel fuels from conventional crudes,
laboratory-blend synthetic diesels and oil blends prepared for
specific properties.

Experimental procedure.

A typical experimental run required 40-60 minutes of
preparation to set the control conditions in the test rig and to
calibrate the analyzers. The actual test procedure started with an
initial burner start-up (cold start), followed by a continuous one
hour run, off for 10 minutes, followed by five 10 minute on/10 minute
off cycles operations. A complete experimental run lasted a total of
170 minutes. The control conditions selected for evaluation of all
the test fuels included the following: fuel temperature of 7°C and
15°C, oil pump pressure of 689 K pascal (100 psi), furnace exit draft
of 0.1 cm (0.04 in) water column, cold air return temperature of 15°C
and fuel firing rate of 2.6 litres per hour (0.65 U.S. GPH). The oil
nozzle used was of the hollow type (NS) with 80° spray angle. The
combustion air supply was set independently for each fuel to obtain a
steady-state smoke number of 2 when tested with a Bacharach smoke
test instrument prior to the run.

Gaseous emissions of O_2, CO_2, CO, NO_x, and hydrocarbons,
along with selected temperatures were continuously monitored during
the entire run. Data acquisition was carefully planned at selected
intervals so that the critical start-up and shut-down transient
emissions were recorded. Particulate emissions were measured during
the start-up transient period using calibrated diesel exhaust smoke
opacity meter (Celesco model 107, Berkeley Instruments) which had
been previously modified for these tests.

Fuel characterization methods.

The analytical techniques used to characterize the fuels include ASTM standard methods for density, viscosity, distillation, flash point, pour point, analine point and aromatic components. Additional techniques used for the determination of aromatics are proton nuclear magnetic resonance (PNMR) for aromaticity and gas chromatography/mass spectrometry (GC/MS) for hydrocarbon compound types.

Proton nuclear magnetic resonance spectroscopy.

Two laboratories were utilized for this analysis. Laboratory 1 used a Varian CFT-20. Laboratory 2 applied a 90 MHz Varian EM-390 spectrometer. Sample to solvent concentration ratios of 50/50 were used to record the spectra. Chloroform $-d_1$ (99.9%) with ME_4Si was used as solvent.

Mass spectroscopy.

A Finnigan 4500 quadropole mass spectrometer was used for MS and GC/MS determinations of PONA and mono-, di-, and poly-aromatic fractions. The samples were separated using a 1.83 m column (3% Dexil 300 on acid washed Chromosorb W) heated from 60°C to 300°C at a programmed rate of 8°C/min. Chemical ionization (methane) mass spectra were acquired continuously during the gas chromatographic separation on a 3 second cycle. The series of peaks characteristic of each given class of compounds - paraffin, naphthenes, and aromatics - were summed continuously throughout the run in characterizing the compound type classes. The olefin content was determined using the PNMR method and any interfering peaks in the mass spectra were corrected. The detailed PONA method is available in the published literature(13).

RESULTS AND DISCUSSIONS

Determination of aromatic components in test fuels.

While it is well known that aromatic hydrocarbons increase particulate emissions and cause related problems in combustion, the method for determining aromatics is not straightforward. The FIA (fluorescent indicator absorption) method is the most widely used standard method (ASTM D 1319) in the oil industry, although it is known to have poor accuracy. Its application is also limited to light distillate oils. GC/MS and NMR methods provide better accuracy and precision but are labour and cost intensive. The industry has

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not completely accepted these sophisticated instrumental techniques since they require specially trained operators and temperature controlled environments. High performance liquid chromatography (HPLC), with its efficient chromatographic column, is known to provide good separation of hydrocarbons but its detection technique is somewhat limited. The two most common detection systems, ultraviolet (UV) and refractive index (IR), are very compound specific to hydrocarbon compound types and require extensive calibration for all compounds present in oils. Therefore, this method is not practical for refinery applications although the instrumentation is less costly and less sophisticated than for GC/MS and NMR. Two detectors considered to be preferable to the UV and IR are the flame ionization detector (FID) and the dielectric constant (DC) detector. As part of the research program described herein, further work is being carried out to develop a nonconventional simple method for determining the aromatics in oils by HPLC with FID detection.

Due to the above discussed variations and limitations involved in aromatic analysis, it was decided to apply several different techniques to determine the aromatic components of the test fuels evaluated in this study. Table 1 shows the aromatic data of 22 test fuels as determined by different techniques. Since it is critical to have accurate fuel property data in establishing the fuel quality/performance characteristics, attempts were made to have duplicate analyses done by independent laboratories whenever possible. Aromatic content is gathered from PONA data using the GC/MS technique. It is defined as the percent of aromatic type hydrocarbons determined on a molecular basis. Aromaticity as described herein represents the percent carbon in aromatic rings or the ratio of aromatic carbons to the total number of carbons (14). It can be determined by proton NMR or carbon 13 NMR methods. Aromaticity data were chosen for duplicate independent analysis since NMR is less dependent on the instrument, operator, and method than GC/MS. Aniline point measurements were made using the ASTM D 611 standard method.

The correlation between different analysis methods can be seen in Figures 2 and 3. The aromatic content and aromaticity data are in good agreement and have a linear correlation coefficient of 0.958. The aniline point data show greater spread (Figure 2) which could be due to the fact that aniline point is not an absolute parameter but only provides a measure of aromatics. As well, aniline point is known to give poor accuracy in the analysis of heavy fuels. The correlation coefficient for the aniline point data is 0.928.

Figure 3 is the regression plot of the FIA and aromatic content data. It shows a positive linear correlation with a correlation coefficient of 0.963. However, the method cannot provide data for some heavy fuels due to incomplete separation in column chromatography.

Figure 4 compares the aromaticity data from two independent laboratories. The slight variation is due to the difference in data manipulation methods used by the two laboratories. Laboratory 1 used

the Brown and Ladner method which assumes that the paraffinic
hydrogen to carbon ratio is exactly 2.0 (15). Laboratory 2 took the
assumption that the hydrogen to carbon ratio is larger than 2.0 and
also incorporated corrections associated with other physical
properties such as density and refractive index (16). The combined
data show good agreement with a correlation coefficient of 0.971.

The physical and chemical properties of all the test fuels are
reported in Table 2. The correlation between physical properties,
e.g. fuel density, and aromatic properties was also studied as
illustrated in Figure 5. Aromaticity and density exhibit a good
linear relation with a correlation coefficient of 0.942. Aniline
point data show wide variation which can be attributed to the reasons
previously discussed.

Significant improvement can be seen in aniline point data
correlation when it is related to the K factor of the fuels. K
factor, also known as the Watson characterization factor, is defined
as

$$K = \frac{(T_{b,R})^{1/3}}{s}$$

where $T_{b,R}$ = molal average boiling point, $^\circ R$

s = specific gravity at 60/60 F (17).

K factor is the most widely used index of composition in the
characterization of petroleum crude oils.

From Figure 6, the improved correlations are 0.979 and 0.963
for aromaticity-K factor and aniline point-K factor respectively.
The improvement is due to the incorporation of boiling points rather
than considering only one parameter: density (specific gravity).
K factor is the most promising parameter for refinery use since it
can be easily calculated from the boiling points and specific gravity
data, which are readily available from fact sheets. As part of this
research study, correlations are being developed to use K factor in
place of fuel aromaticity to predict fuel performance.

Effect of fuel aromatics on soot production.

The effects of fuel aromatic compounds on combustion processes
have been widely studied and are well documented in the literature.
The impact of aromatics on residential oil combustion, especially on
the increased generation of incomplete combustion products (e.g.
particulates, carbon monoxide and hydrocarbons) have been examined
under the research program described herein. Discussion in this
paper is limited to soot production.

In the literature on solid particle emissions from combustion
processes measurements for parameters such as smoke, particulates,

opacity and soot are reported based on the specific methods and
instrumentation used. Particulates, which are generally defined
for regulatory purpose as "any material with the exception of water
that collects on a filter operated in an air-diluted exhaust stream"
require multi-step, time consuming and expensive operations. Soot or
carbon is defined as the nonvolatile portion of particulates and can
be measured by thermogravimetric analysis or by the removal of
condensed hydrocarbons from the particulates. Commercial smoke
meters provide smoke opacity or transmittance readings and smoke
testers such as Bosch and Bacharach (ASTM smoke number) offer smoke
numbers. Although these methods all measure some sort of "unburnt
combustion solids", conversion between the various methods is
difficult if not impossible. Attempts at this have been made by
Homan(17) who reports conversion factors among 11 smoke measurements;
Alkidas(18) reported on the relationship between smoke measurements
and particulates.

        In this study, solid particles from furnace exhaust are
measured with a Celesco smoke opacity meter and a Bacharach smoke
number tester. The calibration of the smoke meter, and correlation
with particulate mass concentration, has been carried out and
reported elsewhere (20). Analytical data are reported in terms
of percent opacity for ease of discussion; each reading represents
opacity per transient phase or per cycle. For cyclic operations,
data reported is the mean of a 5 cycle test.

        The analytical precision of the data from opacity measurements
of all test fuels has been discussed in a previous publication(12).
Each value represents the mean of data from a minimum of 3 runs, with
precision expressed as the coefficient of variation. For regular
commercial No 2 fuels, transient emissions show variation of less
than 7%. Heavy and highly aromatic fuels which usually experience
combustion problems, show poor precision with errors usually higher
than 20%. The error increases with decreasing oil quality. The
regression plots in this paper show data from both a wide range of
fuels. The errors associated with the lower grade fuels (usually on
the right hand of the graph) are much larger than for the better
quality oils (data on the left hand side).

        The precision of the data is also affected by the run type.
Transient opacity readings from cyclic operations show better
precision than for cold start trials. This is a direct reflection of
the effect of oil temperature on combustion. Cold start operations
are subject to cold fuel and environment, whereas the subsequent
cyclic starts experience more favourable conditions. For example,
even though for all the experiments reported herein the fuel tank
temperature was maintained at 15°C, the oil temperature at the nozzle
adapter at the beginning of a cold start averaged 17 - 20 °C as
compared to 40 - 75 °C for cyclic runs.

        Opacity readings from cold start and cyclic transient phases
from combustion tests of 22 fuels are reported in Table 4. Figure 7
graphically compares cold start and cyclic data. Aromaticity, being
the most reliable among 4 different parameters, is used as the
measure of fuel aromatic components. The current data indicate an

exponential increase in smoke opacity at cold start ignition for an increase in aromatic components. The breakaway point at 45% aromaticity suggests the upper limit which the fuels can tolerate without excessive emission levels. Opacity readings normally observed from domestic furnaces firing with commercial No. 2 fuels are 1.5% to 2.5% at the cold start transient phase. Cyclic operations generate much lower smoke due to a more favourable combustion environment. The effect of aromatics during normal furnace on/off operation is less pronounced even when oils with considerably high aromatic content are used. The average opacity per cyclic start for commercial furnace fuels is between 0.3% to 0.7%. The worst case observed (1.8% opacity) is for fuel with aromaticity of 59%.

From these observations, it appears that aromaticity is the prime factor causing soot production from residential burners. In reality, the observed combustion characteristics including gaseous and particulate emissions and burner ignition behaviour are caused by several physical and chemical properties, interrelated in a complex manner. For example, the breakaway point at 45% aromaticity, as seen in Figure 7, coincides with the following breakaway points in the applicable plots: 60% aromatic content, 4 c St fuel viscosity and cetane index of 25. Results describing the overall effects of aromatics, viscosity, and other physical and chemical properties on soot production have been reported elsewhere (18). It should be noted that in the opacity - aromaticity regression plots data from fuels with viscosity higher than 3.5 c St are omitted in order to try and isolate viscosity effects. It is impossible to totally isolate the effect of any one parameter on combustion performance, however a general indication of its importance may be drawn.

The research program described in this paper is continuing with the objective of incorporating all of the significant fuel oil properties into a mathematical model which predict combustion performance based on oil properties.

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Table 1. Aromatic Properties of Fuels.

Fuel	FIA %			MS %				Aromaticity %		Aniline point
	A	O	S	P	O	N	A	Laboratory1	Laboratory2	°C
C	45	3	53	24	0	34	42	31	31	45
D	na	na	na	29	0	38	33	24	22	60
E	23	11	66	32	0	43	25	21	19	61
F	na	na	na	21	0	26	42	42	44	31
L	38	1	61	29	0	36	35	21	27	55
M	71	1	28	15	0	20	65	40	48	26
N	29	1	70	33	0	37	30	16	22	57
O	78	2	21	10	0	14	76	51	59	5
P	78	1	22	13	0	13	74	48	54	7
Q	28	1	71	32	0	41	27	15	19	61
R	20	0	82	37	0	40	23	9	16	56
V	32	1	31	31	0	46	28	14	17	46
W	30	1	70	33	0	42	30	15	22	50
X	42	1	57	27	2	28	48	32	42	29
Y	55	2	44	23	1	30	50	34	43	36
Z	34	1	66	31	0	46	27	18	21	57
AA	33	1	67	28	0	51	26	18	23	56
BB	45	4	52	31	0	35	39	28	38	41
CC	59	1	39	25	0	27	54	36	44	30
DD	69	3	28	19	0	21	64	46	53	14
EE	62	2	36	14	0	17	68	45	49	25
FF	31	2	67	35	1	35	29	20	25	56

A, O, S   denotes aromatics, olefins, saturates
P,O, N,A   denotes paraffins, olefins, naphthenes, aromatics
na   denotes not available

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Table 2. Physical and Chemical Properties of Fuels.

Fuel	Density kg/l 15°C	Viscosity c St @ 40°C	Heat of combustion MJ/Kg	Simulated distillation °C 5%		Flash point °C	Pour point °C	Refractive index
				°C 5%	°C 95%			
C	0.88	2.91	44.8	160	387	62	-39	1.50
D	0.86	3.04	46.2	188	357	64	-29	1.48
E	0.86	3.26	46.8	211	351	88	-26	1.48
F	0.92	3.42	44.6	189	421	67	-52	1.49
L	0.86	2.68	44.0	190	404	62	-18	1.49
M	0.93	3.60	42.9	221	359	114	-13	1.53
N	0.85	2.09	44.3	196	357	62	-30	1.47
O	0.95	2.82	42.4	179	309	87	-24	1.55
P	0.94	2.82	43.2	184	316	101	-27	1.54
Q	0.85	2.59	45.5	172	363	63	-29	1.47
R	0.80	1.28	46.2	121	220	`48	-51	1.45
V	0.84	1.74	45.3	94	414	11	-60	1.47
W	0.84	1.88	45.3	134	356	21	-36	1.47
X	0.86	1.35	44.2	127	376	10	-60	1.51
Y	0.91	3.26	43.7	207	380	70	-33	1.52
Z	0.87	4.09	44.8	204	378	72	-33	1.49
AA	0.88	5.12	44.7	211	386	74	-42	1.49
BB	0.88	2.65	44.5	206	332	73	-24	1.50
CC	0.90	2.70	43.9	213	329	78	-36	1.51
DD	0.94	2.77	42.7	224	330	83	-27	1.54
EE	0.92	2.90	43.2	185	380	65	-51	1.53
FF	0.86	2.52	45.1	200	325	70	-30	na

* na denotes not available

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Table 3. Correlation of Fuel Properties and Particulate Emissions.

Fuel	Aroma-ticity%	Aromatic content%	Analine point°C	Diaromatics %(GC/MS)	K factor	Opacity% (cs)	(cy)	Smoke # (cs)	(cy)
C	31	42	45	12	11.29	1.3	0.7	6	6
D	22	33	60	12	11.56	1.6	0.5	8	6
E	19	25	61	6	11.64	1.8	0.6	7	6
F	44	42	31	12	11.01	1.5	2.2	9	7
L	27	35	55	13	11.45	1.9	1.3	7	7
M	* 48	65	26	19	10.81	* 52.3	1.8	>9	7
N	22	30	57	8	11.55	0.7	0.2	6	6
O	59	76	5	44	10.46	16.8	1.9	>9	7
P	54	74	7	30	10.62	9.1	2.1	8	7
Q	19	27	61	5	11.68	1.6	0.4	7	6
R	16	23	56	3	11.79	0.3	0.1	6	4
V	17	28	46	2	11.54	1.6	1.2	8	7
W	22	30	50	5	11.58	2.0	0.6	7	6
X	42	48	29	18	11.21	2.1	1.8	7	6
Y	43	50	36	22	11.03	10.4	1.2	>9	7
Z	* 21	27	57	7	11.52	* 2.4	1.0	>9	6
AA	* 23	26	56	6	11.43	*14.8	0.6	9	5
BB	38	39	41	13	11.22	3.0	1.2	8	6
CC	44	54	30	19	11.01	5.0	2.3	8	7
DD	53	64	14	34	10.61	15.4	1.8	>9	7
EE	49	68	25	na	10.81	20.9	2.9	>9	7
FF	25	29	57	10	11.57	2.3	0.6	5	4

cs denotes cold start
cy denotes cyclic start

• data not used in regression plots as fuel viscosity was higher than 3.6 c St.
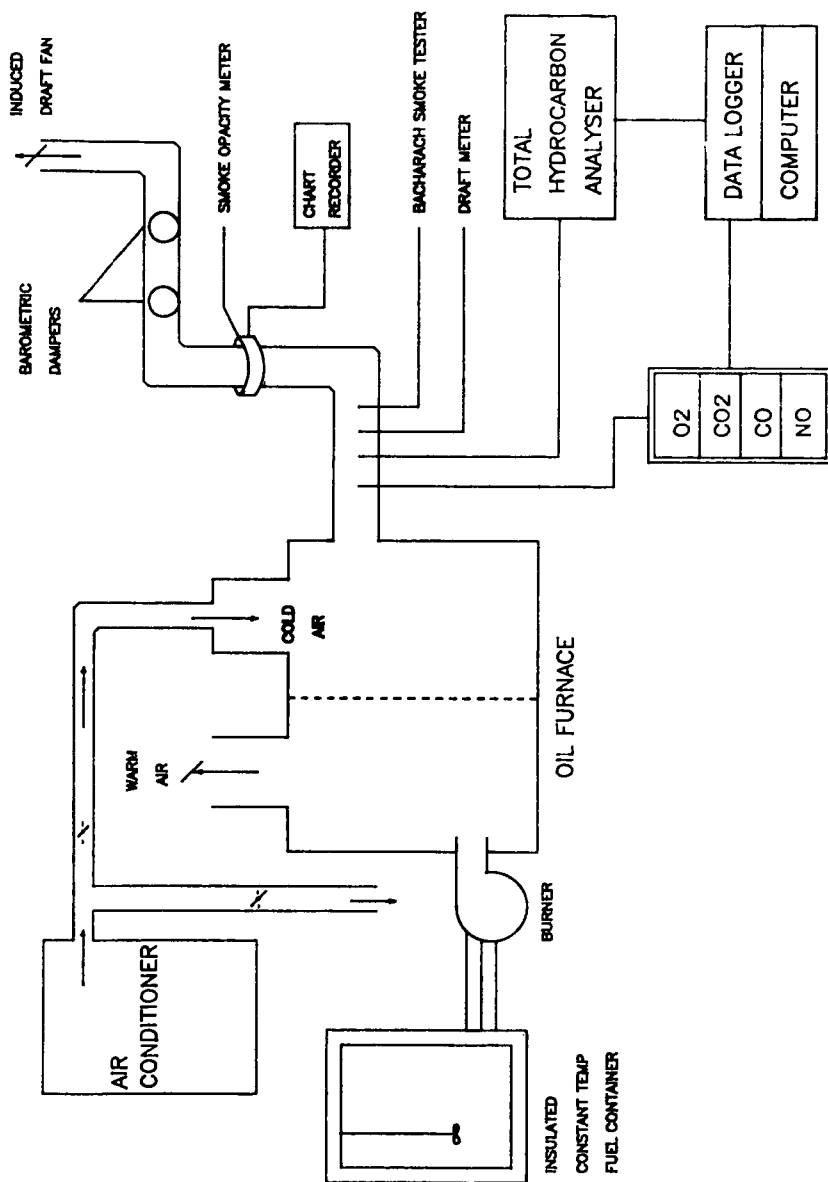
Figure 1. Schematic of the laboratory equipment facility used in the fuel quality evaluation experimental program.

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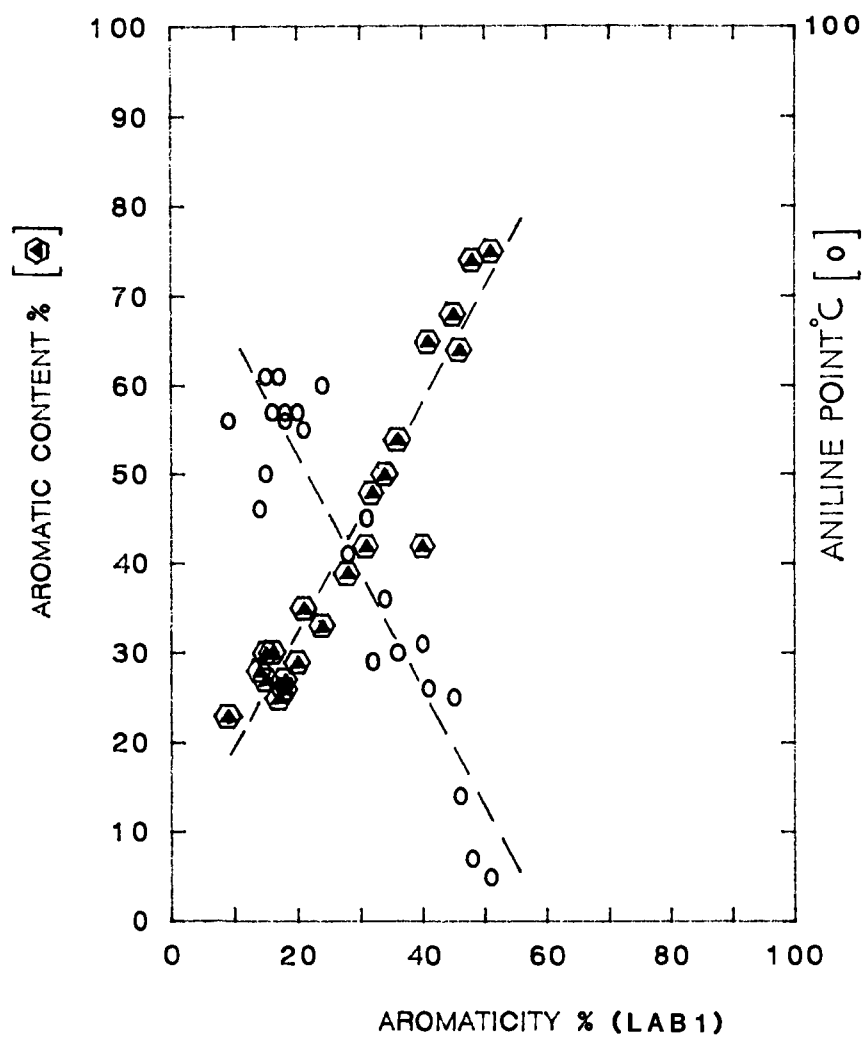
Figure 2. Comparison of fuel aromatic data as determined by
three different analytical techniques.
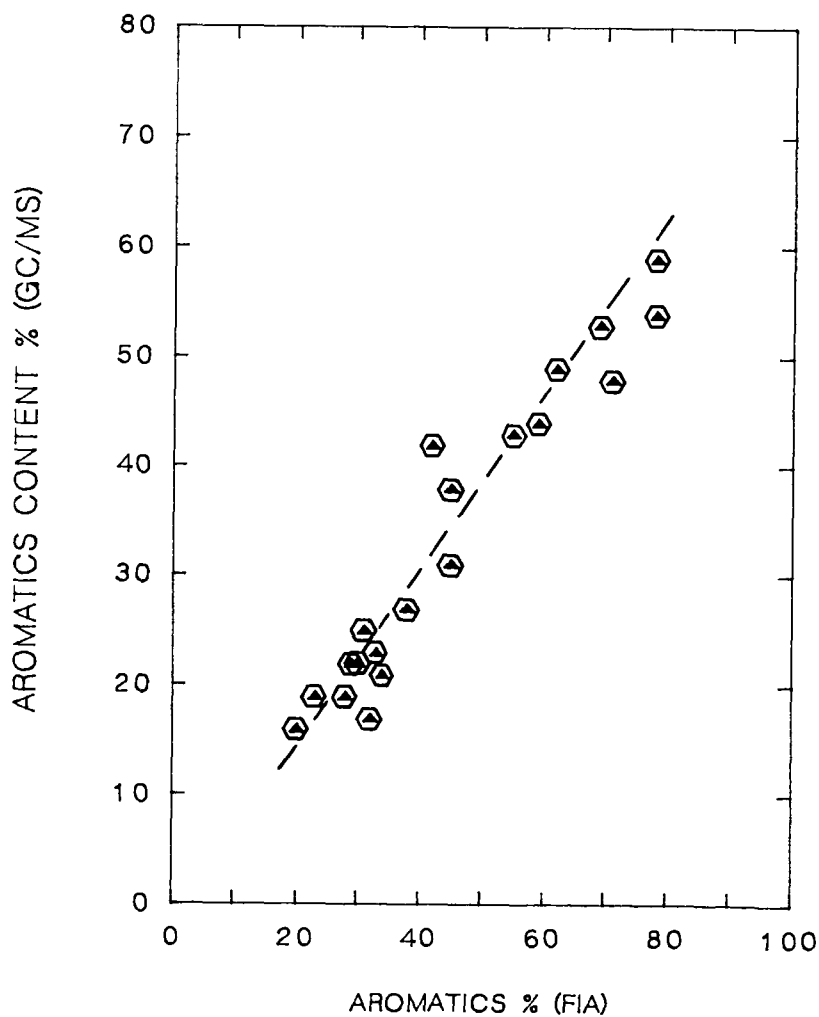
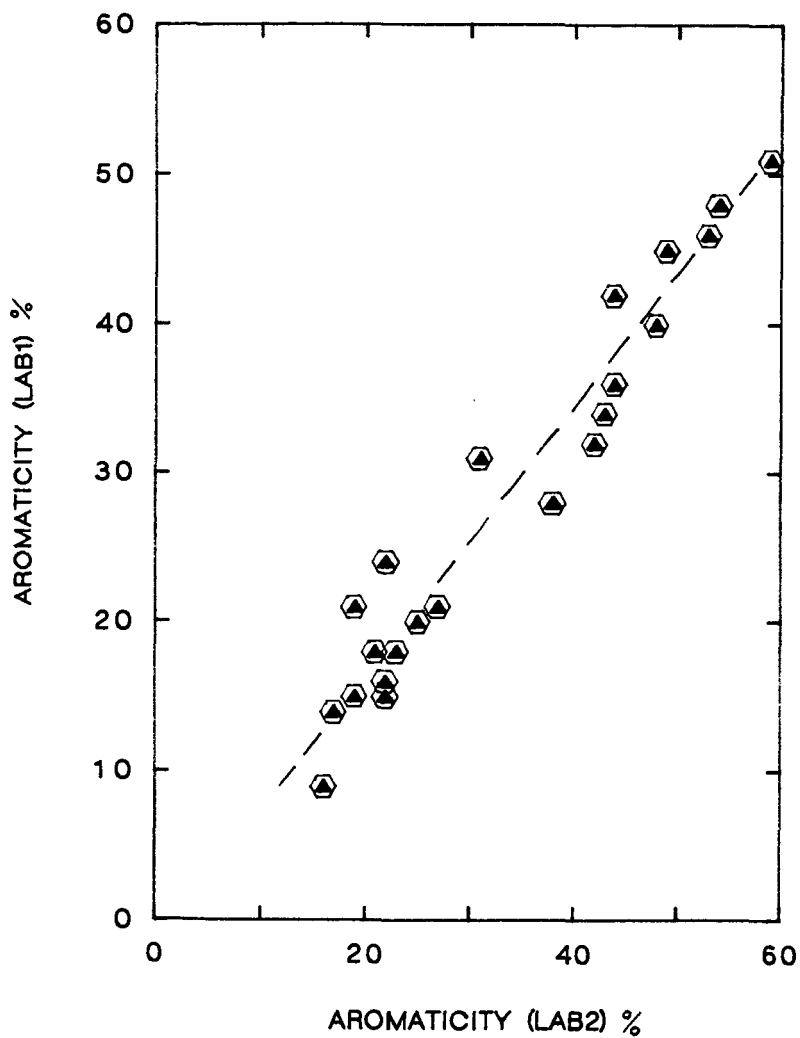Figure 3. Correlation between fuel aromatic data as determined by GC/Ms method and FIA method.

Figure 4. Comparison of fuel aromatic data as determined by two independent laboratories using PNMR technique.
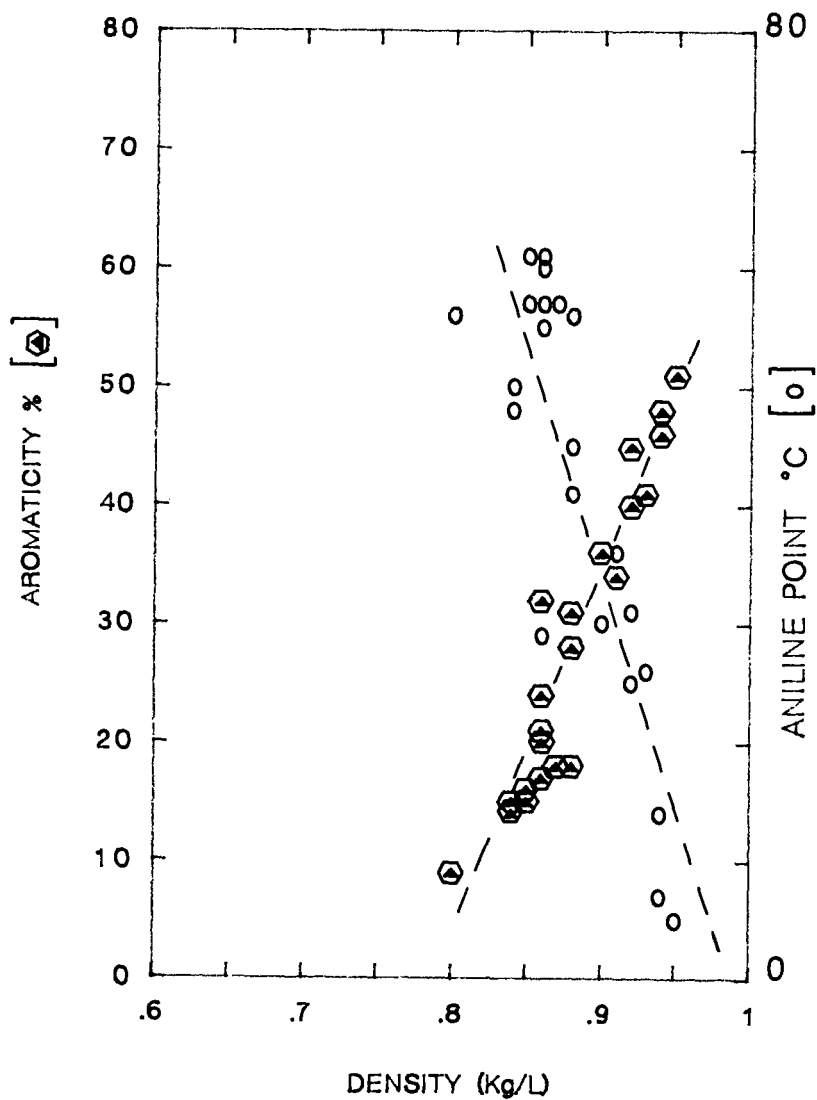
Figure 5. Correlations between fuel density and fuel aromatic
data as determined by PNMR and aniline point
determination techniques.
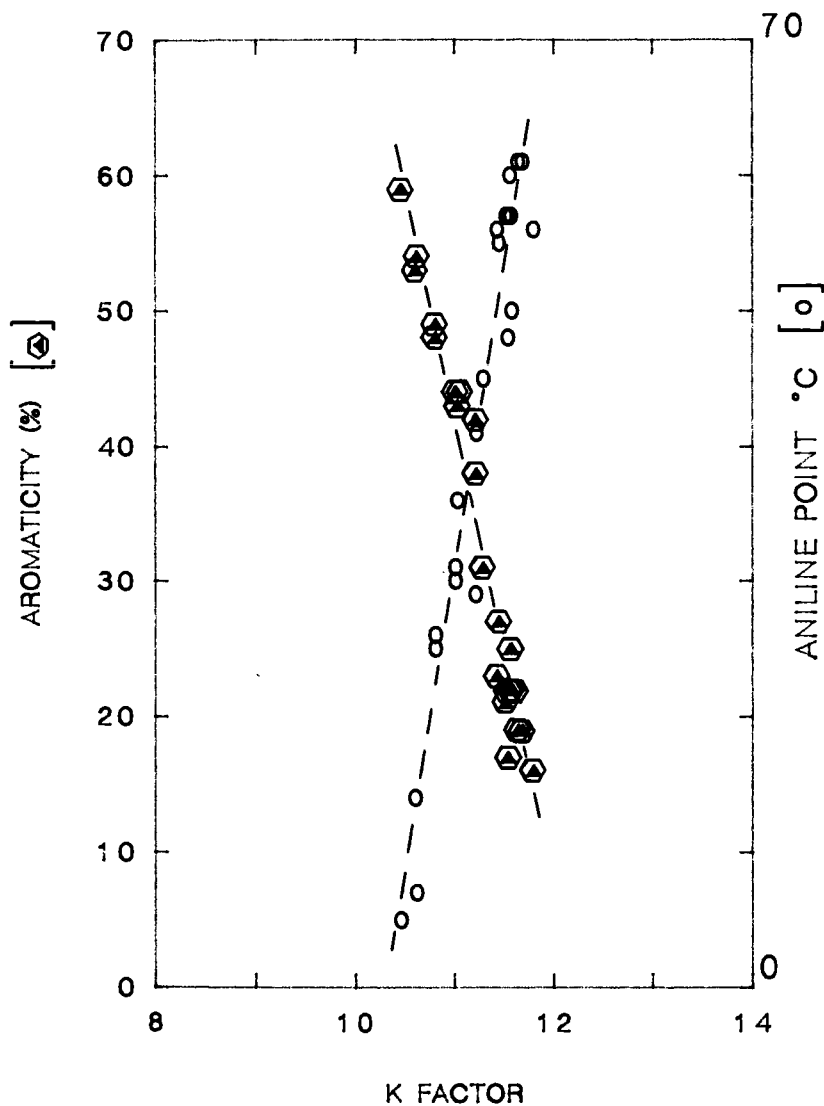
Figure 6. Correlations between Watson K factor and fuel aromatic
data as determined by PNMR and aniline point
determination techniques.
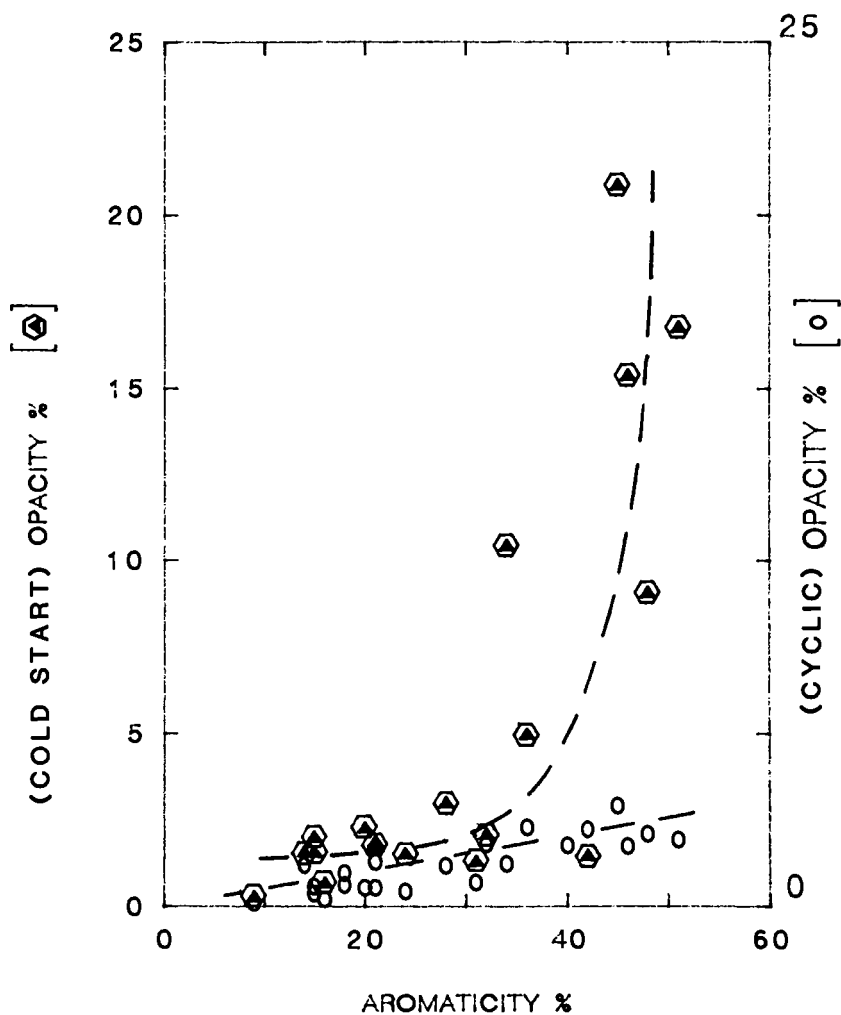
Figure 7. Correlations between fuel aromaticity and transient
smoke opacity from cold start and cyclic operations.

IDENTIFICATION OF ORGANIC COMPOUNDS IN THE BITUMEN
OF CHATTANOOGA OIL SHALE

Chris W. McGowan, Barbara E. Greenwell, David J. Crouse,
Richard Markuszewski[*], John J. Richard[*] and Michael J. Sepaniak[**]

[*]Dept. of Chemistry, Tennessee Tech University, Cookeville TN 38505
[**]Ames Laboratory, Iowa State University, Ames, IA 50011
[*]Dept. of Chemistry, University of Tennessee, Knoxville TN 37996

ABSTRACT

The bitumen of Chattanooga oil shale has been extracted with benzene. The benzene-soluble material was separated into acid, base and neutral fractions with ion exchange chromatography. This separation scheme has been used extensively to separate the organic material in Green River oil shale. The acid fraction was esterified with BF_3/MeOH. A large portion of the acid fraction was not esterified and this material was considered to be phenolic. The bases were separated into two fractions using alumina. The esters, the two base fractions and the total neutral fraction were analyzed using gas chromatography coupled to mass spectrometry. Two series constituting the methyl esters of normal carboxylic acids and carboxylic acids containing one double bond were identified. No homologous series were indicated in the base fraction. The base fraction was highly aliphatic. The major components in the neutral fractions were two series constituting normal and isoprenoid alkanes. A series of cycloalkanes and a series of alkenes were also indicated. The analysis scheme employed functions well for the separation and identification of aliphatic materials.

INTRODUCTION

Several cores of Chattanooga Shale from Tennessee have been extracted with benzene. The benzene-soluble bitumens have been further separated into acid, base and neutral fractions (1). In that study, the bitumen was dissolved in benzene and the acid fraction was absorbed on IRA 904 anion exchange resin. The acids were stripped from the resin by Soxhlet extraction with five percent acetic acid in benzene. In a similar fashion, the bases were absorbed on A-15 cation exchange resin and stripped by Soxhlet extraction with five percent isopropyl amine in benzene. The unabsorbed material constituted the neutral fraction. This separation scheme was adapted from the scheme proposed by Jewell et al. (2) and has been used to separate organic material associated with Green River oil shale (3,4,5). This scheme has been very successful in separating the mostly aliphatic material in Green River oil shale. Chattanooga oil shale, however, has been shown to be highly aromatic (6). The work presented in this paper was performed to identify components of the bitumen of Chattanooga oil shale and to make a comparison of the results to corresponding results for Green River oil shale.

Cooper (7) has extracted a Chattanooga oil shale outcrop in Texas and identified the presence of normal carboxylic acids from C_8 to C_{28} with a maximum at C_{16}. The ratio of even numbered carboxylic acids to odd numbered acids was measured at 1.56. Leddy et al. (8) extracted Antrim oil shale (a similar formation of the same age in

Michigan) with toluene and identified a series of normal alkanes and porphyrins.

EXPERIMENTAL

The acid fractions were esterified using boron trifluoride in methanol as described by McGowan and Diehl (9). Approximately 0.1-g samples of the acid fraction were boiled for five minutes in five mL of 14 percent boron trifluoride in methanol. The esters were extracted with two five-mL portions of pentane. Not all of the organic material was extracted into pentane. The base fraction was placed on an activated alumina column and eluted with hexane followed by benzene thus producing two fractions. The neutral fraction was not separated further.

The esters, the total base fraction and the neutral fraction were initially separated by gas chromatography on a six-foot, 1/8-in Tenax column which was temperature programmed from $100^{\circ}C$ to $350^{\circ}C$ with a flame ionization detector (FID). The esters the two base fractions and the neutral fraction were later separated on a 30-meter DB-5 fused silica capillary column which was temperature programmed from $50^{\circ}C$ to $310^{\circ}C$ with FID detection. Finally the separation was performed using the capillary column coupled to a mass spectrometer. A Finnegan 4000 GC/MS system was used. Mass spectra were recorded for the major peaks in each fraction.

RESULTS AND DISCUSSIONS

The pentane-insoluble organic matter remaining after the esterification process represented a highly polar material. This material was considered to be phenolic. However highly polar esters could also have been present. The presence of inorganic salts in the residue and the high volatility of the produced esters made quantitation of this polar material difficult. Attempts were made to quantitate the amount of weak acids (phenols) in the acid fraction by extraction of the carboxylic acids with $NaHCO_3$ solutions and back extraction after acidification. The extracted materials and residues were very gelatinous and difficult to work with. No conclusive results were obtained. This material was not analyzed further.

The gas chromatograms resulting from the DB-5 column and flame ionization detector for the esters, the hexane-soluble base fraction and the neutral fraction appear in Fig. 1. Three homologous series account for all of the major peaks in the esters of the acid fraction. One of the series was composed of normal alkanes ranging from C_{15} to C_{40} with a maximum at C_{24}. The alkanes were absorbed by the polyvinyl benzene portion of the ion exchange resin and later stripped by the acetic acid/benzene solvent. The major series in the ester fraction was composed of the methyl esters of normal carboxylic acids. Normal saturated carboxylic acids from C_6 to C_{26} were identified with a maximum at C_{16}. There was a definite predominance of the even numbered carboxylic acids to the odd numbered carboxylic acids. The methyl esters of the even numbered normal acids constituted 36 percent of the fraction while the methyl esters of the odd numbered normal acids constituted only five percent. A second series was composed of the methyl esters of normal carboxylic acids containing one double bond. Unsaturated acids from C_{10} to C_{20} were identified with a maximum at C_{18}. The

position of the double bond was not identified in this study. However, the mass spectrum of the methyl ester of the C_{18} unsaturated acid was almost a perfect match with the library generated mass spectrum for methyl oleate. Although not as pronouced as for the saturated acids, there was also a definite predominance of the even numbered unsaturated acids to the odd numbered unsaturated acids. The methyl esters of the even numbered unsaturated acids constituted eleven percent of the fraction while the methyl esters of the odd numbered unsaturated acids constituted four percent. Methyl esters of isoprenoid carboxylic acids were not identified. Methyl esters of aromatic carboxylic acids were not identified.

No clear homologous series of bases were identified. No base was unambiguously identified. The mass spectrum of most the components of the base fraction indicated the presence of alkyl amines. Alkyl amines from C_{15} to C_{26} containing from zero to three degrees of unsaturation were indicated. Five components had mass spectra which indicated highly aromatic systems. One of these was tentatively identified as a C_{18} quinoline (10).

The major series in the neutral fraction was composed of normal alkanes ranging from C_{12} to C_{31} with a maximum at C_{17}. A second homologous series was composed of isoprenoid alkanes ranging from C_{15} to C_{25} with a maximum at C_{19}. Both phytane and pristane were identified. Two other homologous series, together equal in concentration to the isoprenoid series, were composed of hydrocarbons containing one degree of unsaturation. The mass spectra of these compounds indicated a series containing rings and a series containing double bonds. A C_{18} alkane containing a cyclohexyl ring was identified. Cycloalkanes from C_{15} to C_{22} were indicated with a maximum at C_{18}. A C_{17} alkene was identified. Alkenes from C_{13} to C_{20} were indicated with a maximum at C_{17}. Two other homologous series, in very low concentration, were indicated by the gas chromatograms but were not identified by mass spectrometry. There was no even to odd predominance in either of the alkane series, the cycloalkane series or the alkene series. No aromatic compounds were indicated as major components of the neutral fraction.

The major compounds identified in this study were essentially the same as the major compounds identified in Green River oil shale (11,12,13,14,15). The notable exceptions were the presence of isoprenoid carboxylic acids and dicarboxylic acids in Green River oil shale; and the presence of unsaturated carboxylic acids and alkenes in Chattanooga oil shale. The presence of unsaturated acids and alkenes was unexpected and has not been noted previously for Chattanooga oil shale. Unsaturated essential fatty acids, such as oleic acid, were probably present at the time of deposition of both Chattanooga and Green River oil shale. However the conditions of lithification have apparently destroyed the double bonds in the case of Green River oil shale while preserving the double bonds in the case of Chattanooga oil shale.

The major components identified in each fraction in this study were aliphatic in nature. Only a few aromatic bases were indicated. The infrared spectra of each fraction (1) indicated the presence of aromatic material. The separation scheme employed in this study including the fractionation, derivatization and gas chromatography

did an excellent job of identifying aliphatic material. While this
scheme works well in identifying the primarily aliphatic components
in Green River oil shale, the scheme falls short in identifying all
the major components of Chattanooga oil shale. The aromatic material
present in Chattanooga oil shale was not identified. Some of the
aromatic material may have been present in the pentane-insoluble
portion of the esterified acids. It is possible that the aromatic
material in Chattanooga oil shale is present primarily in the
kerogen and not in the soluble bitumen. However this seems
unlikely.

CONCLUSIONS

A series of normal alkanes and a series of normal carboxylic
acids have been identified in the acid fraction of the bitumen of
Chattanooga oil shale. An unexpected series of normal carboxylic
acids containing one double bond has also been identified. There
was a definite predominance of even numbered acids to odd numbered
acids. The base fraction was primarily aliphatic. A series of
normal alkanes, a series of isoprenoid alkanes and a series of
cycloalkanes have been identified in the neutral fraction. An
unexpected series of alkenes was also identified. The separation
scheme employed does not identify any aromatic materials as major
components of the bitumen.

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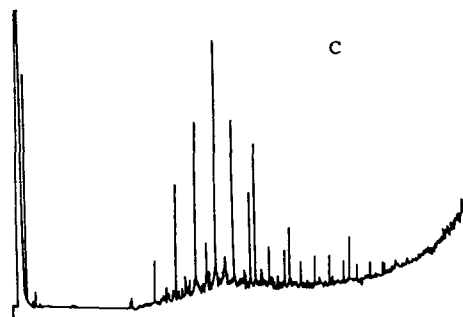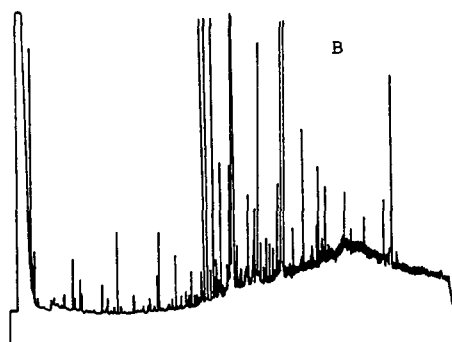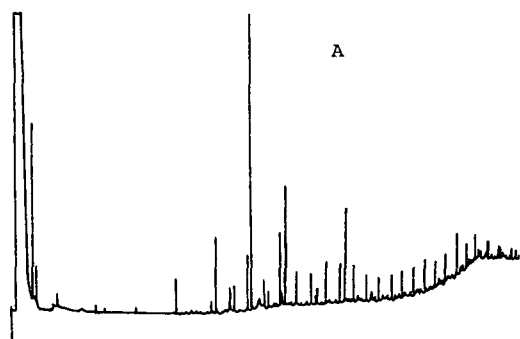
Fig. 1.   Gas chromatograms of A. methyl esters
of acid fraction B. hexane-soluble fraction
C. neutral fraction

SOLVENT SWELLING OF COAL AND COAL MACERALS

David M. Bodily, Jyi-Perng Wann and Vance Kopp

Department of Fuels Engineering, University of Utah
Salt Lake City, Utah 84112

INTRODUCTION

Coal is composed of organic macerals, inorganic mineral matter, pores and pore-filling fluids. Coal normally displays the properties of an amorphous solid, but under appropriate conditions, coal displays both plastic and elastic behavior(1-3). A model to describe the structure of theorganic constituents of bituminous coal is that of a branched/crosslinked polymer. There is no repeating monomer unit, but a unit structure which is covalently bonded by bridging groups. The unit structures are composed of condensed-ring aromatic groups of from 2-4 rings, with molecular weights of around 300. The aromatic rings are substituted by naphthenic rings, alkyl groups and phenolic groups. The bridging groups contain C-O and C-C bonds which are broken during depolymerization and other liquefaction processes. The unit structures cluster in groups which give rise to X-ray diffraction patterns similar to those observed for graphite. The three-dimensional arrangement of the structural units produces a significant micropore volume. In addition to the covalent bridges, polar interactions also serve as crosslinks.

The condensed-ring aromatic units are rigid, but the covalent bridges should provide some flexibility. However, the bonding within clusters of unit structures and the polar interactions reduce the mobility of the coal units and under normal conditions, coal is a glass. At temperatures in the softening range, covalent bonds in the bridging groups are broken and the polar interactions disrupted, providing fluidity to the coal mass. When contacted at room temperature with a suitable polar solvent, coals swell and exhibit plastic and elastic properties(1-3). Under these conditions, the polar bonds are broken and the solvent acts as a plasticizer for the macromolecular network of the coal. Coal passes through a similar state in both carbonization and liquefaction processes, with the solvent being either added vehicle oil or decomposition products of the coal itself. Solvents with Hildebrand solubility parameters in the range of 9-15 (cal/cm3)$1^{/2}$ are effective in swelling coals and, in some cases, inducing spontaneous fracturing(4). The interaction of coal with organic solvents is of interest because of the potential for reacting swollen coals under relatively mild conditions and because of the potential for chemical comminution and chemical cleaning of coals. Changes in the physical properties of coals in the presence of organic solvents are discussed in this paper.

EXPERIMENTAL

Four coals from the Pennsylvania State University Coal Sample Bank and five bituminous coals from Utah were studied. The coals included one anthracite and samples rich in sporinite, resinite, vitrinite and semifusinite. The Utah coals cover a range of response in flotation experiments from easily and quickly floated to difficult to float.

The method of Green et al.(5) was used to measure the swelling properties of the coals. The coal sample was centrifuged in a narrow tube. Solvent is added and the coal is allowed to swell. After

equilibrium is achieved, the coal and solvent are again centrifuged. The increase in height of the column of coal is taken as the volumetric swelling of the coal. This method is reported to be more reliable than gravimetric methods and does not require corrections for pores.

Surface areas of coals and solvent-treated and heat-treated coals were measured by carbon dioxide adsorption at $-77^{\circ}C$. The samples were placed in a vacuum system and any solvent was removed. The amount of CO_2 adsorbed was determined as a function of the pressure and the Dubinin-Polanyi equation was used to determine the surface area/pore volume[6]. X-ray diffraction measurements were performed at room temperature after solvents were removed at lower temperatures. The assignment of the 002 peak in the diffraction pattern was by comparison with the diffraction pattern of graphite.

Maceral fractions were prepared by the density gradient centrifugation method of Dyrkacz and Horwitz(7). The coal was ground in a fluid energy mill to an average particle diameter of several microns. The sample was then introduced into a density gradient of CsCl in water in a centrifuge and dispersed throughout the gradient. The gradient is displaced from the centrifuge and fractions of different density collected. The sample is recovered and a plot of yield versus density provides a density distribution for the sample. Fractions of similar density were combined for further measurements.

RESULTS AND DISCUSSION

The swelling ratio for coal PSOC-297 is shown in figure 1 as a function of the solubility parameter of the solvent used to cause swelling. This coal is 63% vitrinite and 16% sporinite. The swelling behavior is similar to that observed for the other bituminous coals, although the magnitude of the swelling varies from sample to sample. The swelling is expected to be a maximum for solvents that have solubility parameters similar to that of the coal. The curve shows two maxima. Pyridine causes the most swelling of the solvents tested. The effectiveness of pyridine in swelling the coals is thought to be due to the disruption of polar bonds between segments of the coal molecule, replacing them with H-bonds between the pyridine and the coal. The second maximum in the swelling curve is observed for THF as the solvent. The solubility parameter for coals is expected to be closer to that for THF than for pyridine. The less polar solvents may be causing the coal to swell within the constraints of the hydrogen bond crosslinks, without appreciably breaking the crosslinks.

The swelling is greatest for coals with higher vitrinite content among coals of similar rank. The coals with high inertinite and exinite contents show reduced swelling, although the behavior with regard to solubility parameter is qualitatively the same. The inertinite fraction is not expected to swell appreciably. The anthracite sample did not show any swelling in any of the solvents. The behavior of the anthracite and the inertinite fractions is expected to be similar. A separated sample of resinite showed high solubility in the more polar solvents. It is not certain whether a true solution was formed or if it was a gel or colloidal suspension. Swelling measurements could not be made on the resinite.

Swelling for the less-polar solvents does not appear to be the equilibrium swelling since the structure is constrained by the crosslinks and the less polar solvents are not strong enough to break these crosslinks. Samples were swollen with mixtures of THF and

cyclohexane. Swelling for the mixtures was intermediate between the values observed for the pure solvents. When the sample was swollen with THF and diluted with cyclohexane, the swelling remained near that of pure THF for dilutions up to 75% cyclohexane. Once the macromolecular network is expanded by the good solvent, the poorer solvent will maintain the swelling. Swelling would be expected to increase the pores in the coal structure. Surface areas for coals and swollen coals are shown in figure 2. The surface area is related to the pore volume. The surface area for non-swollen coals is 230-250 m^2/g. as measured at -77°C, for samples that are heat-treated up to 400°C. If the heat-treated samples are swollen in methanol and the solvent removed at low temperatures, the surface areas increase to 300-350 m^2/g. The polar solvent is more effective than temperature in causing the network to swell. If the sample is swollen and then heated to 100°C the macromolecular network relaxes and the surface area is similar to that for non-swollen coals. The coals with enhanced porosity show the same x-ray diffraction patterns as non-swollen coals. The solvent apparently does not disrupt the stacking of the condensed-ring aromatic structures in the coal.

CONCLUSIONS

The swelling of bituminous coals as a function of solubility parameter of the solvent shows two maxima. One is attributed to the solvation of the macromolecular network by a solvent with solubility parameter similar to the coal, increasing the hydrodynamic volume of the network. The other maxima is attributed to the breaking of hydrogen bonds that serve as crosslinks by polar solvents. The coal appears to be held in a constrained state by the polar crosslinks. Solvents are more effective in breaking these restrains than temperature. Porosity can be increased by swelling coals and removing the solvent at low temperatures. The coal network has considerable flexibility below 100°C, as evidenced by the relaxation of the induced porosity upon thermal treatment. Inertinite macerals and anthracites show little swelling. Vitrinites show high swelling and exinites show enhanced solubility.

ACKNOWLEDGMENTS

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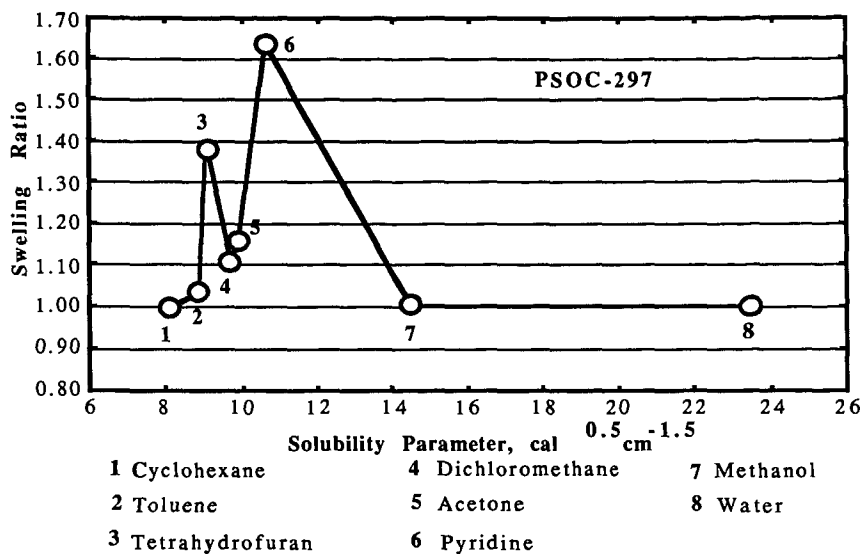7. Dyrkacz, G. R., and Horwitz, P., Fuel, 1982, 62, 3.

1 Cyclohexane   4 Dichloromethane   7 Methanol

2 Toluene   5 Acetone   8 Water

3 Tetrahydrofuran   6 Pyridine

Figure 1 Coal Swelling in Different Solvents

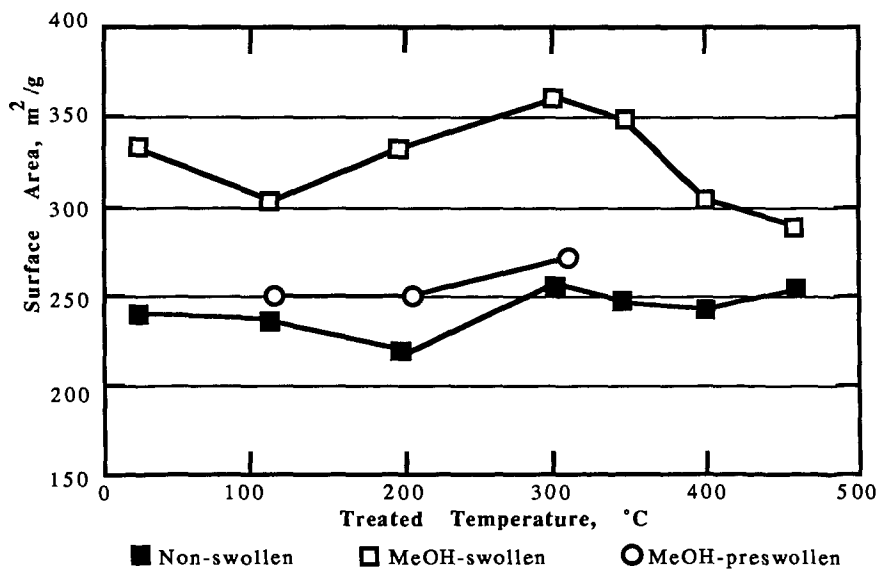■ Non-swollen   □ MeOH-swollen   ○ MeOH-preswollen

Figure 2 Surface Area of Treated Coal

Coal Samples Available from the Premium Coal Sample Program

Karl S. Vorres and Stuart K. Janikowski

Chemistry Division, Building 211
Argonne National Laboratory
9700 South Cass Ave.
Argonne, IL 60439

INTRODUCTION

The purpose of the Premium Coal Sample Program (PCSP) is to provide the basic coal science research community with long term supplies of a small number of premium coal samples that can be used as standards for comparison and correlation. The premium coal samples produced from each coal and distributed through this program are chemically and physically as identical as possible, have well characterized chemical and physical properties, and will be stable over long periods of time. Coals are mined, transported, processed into the desired particle and sample sizes, and packaged into environments as free of oxygen as possible. Humidity is also to be controlled to keep the coals as pristine and in as stable a condition as possible.

There had been a feeling that such a program was needed for quite some time (1,2,3). Different authors and workers have expressed a concern over the difficulty in obtaining well selected, collected, prepared and characterized samples over a long period of time. The variation in properties through a coal seam over relatively short distances and the sensitivity of coal samples to oxidation in typical sample containers lead to difficulties in attempts to reproduce the work of other coal researchers. The PCSP is intended to relieve these concerns.

A number of steps are involved in the preparation and distribution of coal samples. These include selection, collection, transportation, preparation or processing (including mixing and packaging), storage, characterization, shipping and data dissemination. Each of these is necessary, and it one of the goals of the PCSP to provide the best quality possible in each of the steps to ultimately provide the best quality samples that can be distributed. Accordingly considerable care and planning has gone into each of the steps mentioned.

SAMPLE SELECTION

The support from the Chemical Sciences Division of the Office of Basic Energy Science will provide for a suite of eight samples. These samples are to provide as broad a range of representation as possible of U. S. coals. The choice of samples has involved a

consideration of the chemical composition, specifically the carbon, hydrogen, sulfur and oxygen contents to obtain representatives of the important ranges available. After consideration of the chemical composition, some specific coals were selected. These include a North Dakota lignite, Wyoming subbituminous, Illinois #6 high volatile bituminous, Upper Freeport medium volatile bituminous, Pocahontas low volatile bituminous, and a Pittsburgh #8 bituminous coal. Other coals are still under consideration for the remaining two samples.

SAMPLE COLLECTION

Sample collection must take place in an active commercial mine to assure the "freshest" coal possible. The collection is done under the supervision of at least one person from the U. S. Geological Survey. Either or both of Drs. Blaine Cecil and Ron Stanton supervise the collection of the whole seam or channel sample. For an underground sample, a continuous miner is used to expose a fresh seam face. When possible the miner is used to isolate a wedge shaped or rectangular block of coal. After roof bolting the floor around the sample is cleared and plastic sheets are put down to collect the actual sample. A three man crew from the Pittsburgh Testing Laboratory at Homer City, Pennsylvania led by David Allen uses hand picks to remove the sample. Coal is placed in double plastic bags in thinner seams (less than 5' thick), tied and taken to the surface for transfer to 55 gallon stainless steel drums. For thicker seams, the drums are taken directly into the mine, and the samples are shoveled carefully into the drums. Typical collection periods are 3-4 hours from the beginning of the collection to arrival of the sample at the surface.
A core sample was taken for the thick subbituminous sample. A contractor was obtained to provide three cores. A 3" core was taken for the USGS log, another 3" core was obtained to provide chunks of coal for long term storage, and a 6" core was used for the coal to be processed. Cores were rinsed and loaded into drums in the same manner as coal from thinner seams.

TRANSPORTATION

A refrigerated semi-truck is used to transport the sample to ANL for processing. The truck loads the empty drums, cylinders of argon used for purging and other necessary equipment at ANL. This load is taken to the mine site. At the mine the plastic bags of coal are dumped into the drums or the full drums are placed on the truck. The drums are purged with 10 or more volumes of argon gas to reduce the oxygen concentration in the drums to below 100 ppm. The load is then taken directly back to ANL for processing. Typically the sample arrives at ANL within 24 hours after being loaded on the truck. The truck temperature is kept at about 42 F en route.

PROCESSING

A unique facility has been built at ANL to process the coal samples. It is a large glove box about 12' tall, 5' wide and 40 feet long. There are 70 pairs of long rubber gloves in the walls of the box to permit manipulation of the sample and equipment during the processing. The oxygen concentration is maintained below 100 ppm during the processing through the use of a catalytic system to combine hydrogen with impurity oxygen.

At ANL the truck is unloaded and drums are taken to the processing facility with a forklift, weighed and placed in groups of three into an initial airlock. After purging the airlock, the drums are opened, and rolled on casters to a hydraulic drum dumper. The dumper picks the drums up and pours the contents into a crusher. The coal is broken into pieces no larger than 1/2" thick. The crushed coal passes through a chute to a vibrating lift which raises the coal to the top of the box for feeding to a pulverizer. Initially the pulverizer grinds the coal so that the particles pass through a 20 mesh screen. The ground coal is accumulated in a Littleford blender with a 2000 liter capacity. This will hold one ton of coal. After the entire batch has been ground it is then thoroughly mixed in the blender. Special studies were carried out to establish the mixing characteristics with coal samples and set the required duration of mixing. The mixed coal is moved from the blender with a tubular conveyor to either a discharge chute used to fill 5 gallon pails for transfer to the initial airlock for regrinding to pass a 100 mesh screen or to fill 5 gallon borosilicate glass carboys for long term storage. Intermittently portions of the sample are conveyed to an ampoule filler-sealer. Here amber borosilicate vials are filled with either 10 grams of -20 mesh material or 5 grams of -100 mesh material. A hydrogen-oxygen torch is used at stoichiometric flame conditions (controlled with a gas mass flow controller) for the sealing.
In processing,it is planned to prepare 5,000 of the 10 gram ampoules of -20 mesh material and 10,000 of the 5 gram ampoules of -100 mesh material. About 80% of the coal is stored in carboys which can be used later to fill additional ampoules when the supply is depleted.

STORAGE

The ampoules and carboys are kept in a separate storage room at about 72 F. This room is usually dark.

CHARACTERIZATION

The samples are characterized for three purposes. The first purpose is homogeneity determination. Initially, samples taken during the filling of the pails, carboys and ampoules are placed in holders for irradiation in the University of Illinois TRIGA reactor. The disintegration rates of induced Na, K and As are measured for bituminous coals, while the Na, As, La and Sc were used for the subbituminous coal due to the limited amount of K. The rates are compared for the different samples to establish the

homogeneity of the samples. The second purpose for characteriza-
tion is the establishment of the analytical qualities of the
coal. Samples are then analyzed in an interlaboratory program
that is ongoing. Information on the program is available from
the Program Manager. Additioal participation is possible.
Standard ASTM methods or known variations of these are used. The
analyses include the ultimate (C,H,N,S), proximate (volatile
matter, fixed carbon, ash and moisture), calorific or Btu values,
sulfur forms, major and minor elements in the ash, and equi-
librium moisture. Maceral analysis and vitrinite reflectance are
also carried out. For bituminous coals the free swelling index
and Gieseler plasticity are also determined. The third type of
analysis is used to establish the stability of the samples. The
Gieseler plasticity is used as a sensitive indicator of oxidation
for the bituminous samples. This test is done for the initial
coals and is repeated periodically to establish the constancy of
the values. For non-bituminous coals other techniques are being
used and developed. The slurry pH is used to establish the
oxidation which results in conversion of pyrite to sulfate.

AVAILABLE COAL SAMPLES

1. The first sample is an Upper Freeport sample collected near
Homer City Pennsylvania in January 1985. This is a medium
volatile bituminous coal from a 4' thick seam at the point of
collection. The sample characterization is continuing. The
preliminary values are: (as received basis)

      carbon: 74-75%
      hydrogen: 4-5%
      total sulfur: 2-3%
      ash: 12-13
      moisture   1-2%
These samples are available in 5 grams of -100 mesh or 10 grams
of -20 mesh material.

2. The second sample, a subbituminous coal from the Wyodak seam,
was collected about six miles northeast of Gillette, Wyoming in
October, 1985. The seam is about 120' thick at the point of
collection. In this case the sample for processing consisted of
a 6" core through the entire seam. The preliminary analysis of
the sample on an as-received basis is:
      carbon: 63-64%
      hydrogen: 4-5%
      sulfur: 0.4-0.6%
      moisture: 28-30%
      ash: 6-7%

Due to the high moisture content of this sample, it is being of-
fered only in -20 mesh size, in 5 and 10 gram ampoules.

3. The third sample is a high volatile bituminous coal, from the
Illinois #6 or Herrin seam, and was collected about 60 miles
southeast of St. Louis in December, 1985. The 55 gallon drums

used for transporting the samples were taken into the mine since
the seam thickness was about 7'. The preliminary analytical
values on this coal (on an as-received basis) are:

carbon:	61-62%
hydrogen:	4-5%
sulfur:	4-5%
ash:	15-16
moisture:	9-10

This material is being offered in 5 grams of -100 mesh and 10
grams of -20 mesh coal.

4. The fourth coal is a Pittsburgh #8 seam sample from about 60
miles south and west of Pittsburgh, Pennsylvania. This was col-
lected in March, 1986. The seam was about 6' thick at the collec-
tion point. The sample drums were taken into the mine to
facilitate the loading and purging of the drums on the surface.
This sample is being offered in ampoules of 5 grams of -100 mesh
and 10 grams of -20 mesh material. The preliminary analytical
data for the as-received samples were not available at the time
of the writing.

SAMPLE AVAILABILITY

Samples are available to researchers upon completion of an order
form. These forms are available from the Program Manager, Dr.
Karl S. Vorres, at the address given in the heading, or by call-
ing (312) 972-7374, or FTS 972-7374. The order forms accompany
the periodic Product   Announcements.   These announcements
briefly describe the sample in terms of its source and type of
coal. When available, initial analytical data is included. In-
dividuals may request that they be placed on the mailing list to
receive these announcements by writing the Program Manager, in-
dicating their address, telephone number and research interests.
Upon receipt of the order and payment in the Assistant
Controller's office, the orders are transmitted to the Program
Manager for packing and shipping. A nominal replacement charge,
currently $1.60 per gram, is made for the samples. An additional
charge is made for foreign shipment to defray the added shipping
charges. Samples are normally sent by United Parcel Service.
Samples are shipped in specially designed corrugated cardboard
cartons with foam padding above and below the ampoules, and an
air space around the outside of them.

Samples are available in reasonable quantities. The Program
Manager reserves the right to limit quantities in order to
provide a continuing supply to all workers in the field over a
decade or more.

USERS ADVISORY COMMITTEE

A Users Advisory Committee serves to provide a range of comments
and suggestions on the Program to maximize its value to the users
community. The individuals come from a range of backgrounds to

permit a variety of input on the many aspects of the sequence of events from the sample selection through distribution. The initial Committee included: Drs. Blaine Cecil of the U. S. Geological Survey, Marvin Poutsma of Oak Ridge National Laboratory, Ronald Pugmire of the University of Utah, William Spackman of Pennsylvania State University, Irving Wender of the University of Pittsburgh, Randall Winans and John Young of Argonne National Laboratory. The committee does rotate after a period of time. Newcomers to the group are: John Larsen of Lehigh University and Leon Stock of the University of Chicago. The Program Manager is deeply appreciative of the counsel and suggestions given by this group.

CURRENT RESEARCH

A wide range of programs is making use of the samples. Some examples include: new methods for direct determination of oxygen and organic sulfur in the coal matter, new methods of characterization using inverse chromatography, solvent swelling studies, reactions of organic sulfur species in the coal. A number of proposals to different funding agencies have specified that the investigators were planning to use these samples in their work.

ACKNOWLEDGMENTS

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